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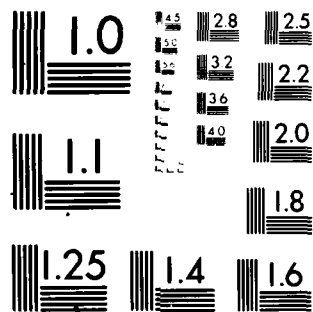
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## LIQUID CRYSTAL MATERIALS FOR MATRIX DISPLAYS

J. David Margerum and Anna M. Lackner

Hughes Research Laboratories

3011 Malibu Canyon Road

Malibu, CA 90265

April 1981

Contract N00014-79-C-0524

Technical Report No. 1

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TECHNICAL REPORT NO. 1

Liquid Crystal Materials for Matrix Displays

by

J. David Margerum and Anna M. Lackner

Hughes Research Laboratories  
Malibu, California

April 2, 1981

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Studies are made on improved liquid crystal (LC) materials for use in MOSFET matrix displays operated with dc-activated dynamic-scattering (DS). The results provide a basis for development of nematic LC materials capable of wide-temperature-range storage, dc operation at elevated temperatures (35° to 71°C), and long lifetime displays. LC structural effects are evaluated by using different combinations of components from eight classes of esters, including phenyl benzoates, phenyl		

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thiobenzoates, phenyl cyclohexanecarboxylates, phenyl acyloxybenzoates, a phenyl benzoyloxybenzoate, and a phenyl biphenylcarboxylate structure. Six mixtures are characterized at 25°C, and their viscosity, dielectric anisotropy, conductivity anisotropy, and dc-activated DS effects are studied at elevated temperature. Three mixtures are thermally stable at 100°C in evacuated tubes, with redox dopants present. Their dc-DS stability is studied at 55°C, both in transparent cells and in cells with reflective metal electrodes. Correlations from these studies provide a good basis for further optimization of LCs for matrix displays. However, additional studies are needed on thermal instability problems caused by reactions with glass surfaces and with organic sealants in display cells at elevated temperatures.

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## SECTION 1

### INTRODUCTION AND SUMMARY

#### A. INTRODUCTION

The goal of this program is to develop liquid crystal (LC) materials and techniques suitable for use in MOSFET matrix displays<sup>1-4</sup> such as those being developed by Hughes Aircraft Company for several military applications, including an integrated head-up airplane cockpit display, a helmet-mounted display, a color alphanumeric display, and a flat panel status advisory display. The key LC material problems are related to the requirements that these military displays must be storable over a wide temperature range (about  $-60^{\circ}$  to  $80^{\circ}\text{C}$ ) and must be operable in ambient temperature ranges between about  $-50^{\circ}$  and  $71^{\circ}\text{C}$ . Because it is much easier to heat LC displays than to cool them, and also because fast response times (up to TV rate) are needed, our program is aimed especially at the use of LCs in the upper part of the operational range. Thus, our goal is to have displays that are operable up to  $71^{\circ}\text{C}$  from ambient heating, and that are heated to a minimum cell temperature (probably in the  $25^{\circ}$  to  $40^{\circ}\text{C}$  range) when the ambient conditions are not warm enough.

The LC electrooptical technique that has been used in the Hughes matrix display is the dc-activated dynamic-scattering (DS) mode.<sup>5</sup> Redox dopants<sup>6-10</sup> are used in phenyl benzoate LCs to give efficient scattering at relatively low voltages, and to permit long operational lifetime capability in the dc mode at room temperature. These dopants provide adequate conductivity, and conductivity anisotropy<sup>11,12</sup> for dynamic scattering. And they also protect the LC by carrying essentially all of the current through the cell, by means of the electrochemical reversibility of their oxidation and reduction reactions. A key problem is that the resistivity of the LC must be maintained within a range that is not too high for adequate dynamic scattering, and is not so low that the charge on each pixel electrode leaks off too fast compared to the

update frame rate. At an update rate of 30 times/sec, the room temperature resistivity of the LC should be between about  $10^9$  and  $10^{10}$   $\Omega$ -cm. Because of strong temperature dependence, typical LCs have to be maintained within about a 30° range (e.g., 40 to 71°C) to control their resistivity within this range. Other key problems include the thermal stability of LCs in cells at high storage temperatures, electrochemical stability at warm operating conditions, sealant contamination effects on resistivity and surface alignment, heating and cooling effects on alignment stability, and adequate response times at various temperatures. Despite these problems, the dc-activated dynamic scattering mode appears the best technique for obtaining TV rate images with gray scale in the matrix display.

#### B. SUMMARY OF RESULTS

The research studies of this contract are directed toward improved LC materials for use in MOSFET matrix displays which are operated with redox dopants for dc-activated DS effects. The main objective is to provide a basis for the development of nematic LC materials capable of wide-temperature range storage (-60° to 80°C), dc operation at elevated temperatures (40° to 71°C), and long lifetime displays. Candidate LC mixtures with a variety of components are selected and studied in regard to structural effects on their anisotropic, DS, and thermal stability properties. Most of these studies are described in a paper submitted for publication. (See Appendix A.) Correlations from these studies provide a good basis for further optimization of LC materials for matrix displays.

The effects of components on the anisotropic and electrooptical properties of LC ester mixtures were studied in regard to their use in matrix displays. Studies were made on six eutectic mixtures previously formulated at Hughes. They all have relatively wide nematic ranges, similar clearpoint temperatures, and each mixture contains a different combination of components from eight classes of LC ester structures.

Studies are made on low temperature crystallization, on birefringence ( $\Delta n$ ), flow viscosity ( $\eta$ ), dielectric anisotropy ( $\Delta\epsilon$ ), and conductivity anisotropy ( $\sigma_{\parallel}/\sigma_{\perp}$ ), as well as their DS properties of threshold voltage ( $V_{th}$ ), time responses ( $\tau$ ), and scattering angles at 25°C. The results in these areas include the following observations:

- The mixture with the best low temperature stability has a nematic range of from -20° to 76°C.
- The mixture whose components include esters of acyloxybenzoate or biphenylcarboxylate structures have higher nematic melting points than the calculated eutectic values.
- Birefringence is relatively higher with the use of thiobenzoate esters, and  $\Delta n$  is lower with the use of cyclohexanecarboxylate esters.
- Viscosity is relatively lower with cyclohexanecarboxylate components, and  $\eta$  is higher with benzoyloxybenzoate diesters, with biphenylcarboxylate esters.
- Mixtures with lower  $\eta$  are advantageous because the DS turn-on time ( $\tau_{on}$ ) and decay time ( $\tau_D$ ) are faster.
- The DS- $V_{th}$  depends on the surface alignment,  $\sigma_{\parallel}/\sigma_{\perp}$ , and  $\Delta\epsilon$  of the redox-doped mixtures. In surface- $\parallel$  cells (i.e., LC aligned parallel to the surface) of similar  $\sigma_{\parallel}/\sigma_{\perp}$ , the  $V_{th}$  increases as  $\Delta\epsilon$  becomes more negative.

The characteristics of the LC mixtures were studied at elevated temperature, including temperature effects on  $\Delta\epsilon$ ,  $\sigma_{\parallel}/\sigma_{\perp}$ ,  $\rho$ (resistivity),  $\eta$ , DS efficiency, and DS response times. The results include the following observations and conclusions:

- The mixtures show some cybotactic nematic character (i.e., short range smectic order) near or above room temperature. Revised compositions with less cybotactic effects should have better DS characteristics, particularly in the 25° to 45°C range.
- The dc-DS curves (scattering versus voltage) are not strongly affected by elevated temperatures. Heated cells show improved scattering levels below 10V, but above 55° they show poorer scattering above 10V as compared to DS at 25°C.

- The dc-DS  $\tau_{on}$  is about 2 to 3 times faster at 60° than at 25°C. This is favorable for the operation of MOSFET matrix cells at elevated temperatures, since the problem of charge leakage of the dc signal through the heated LC mixture would be minimized if the display cell was fully activated in a fraction of a 33 ms frame time.

The thermal stability of the LC mixtures were studied at an accelerated condition of 100°C in various types of containment. These included studies of undoped samples in evacuated tubes, in crimp-sealed DSC (differential scanning calorimetry) aluminum pans, and in both sealed and unsealed thin test cells with conductive glass windows. Samples with added redox dopants (dibutylferrocene and 2,4,7-trinitro-9-fluorenylidene malononitrile, abbreviated as DBF/TFM) were studied similarly, but not in DSC pans. The results include the following observations and conclusions:

- Three mixtures have excellent long term stability at 100°C in evacuated tubes, while the other three mixtures show decomposition effects in the presence of the DBF/TFM redox dopants. The thiobenzoate and biphenylcarboxylate components are the source of these thermal instability effects.
- All of the mixtures show decomposition effects at 100°C when used as thin LC layers in unsealed glass cells, even in a nitrogen-flushed oven. High melting crystalline products are formed, and the reactions are catalyzed by both glass surfaces and traces of oxygen.
- Mixtures heated at 100° in evacuated glass test cells sealed with epoxy adhesives show some thermal degradation effects, mainly due to conductive impurities from the sealant.

The electrochemical stability of redox-doped mixtures was studied in sealed and unsealed cells at 55°C, using the three mixtures with the best thermal stability. These studies include the following results:

- Unsealed cells at 55°C show no serious defects until after 1500 hr at 20 V dc. More stable resistivity levels are shown in cells with one reflective silver (negative) electrode than with two conductive glass electrodes.
- Sealed cells at 55°C show rapid degradation at 20 V dc, due to conductive impurities picked up by the LC from the sealant.

### C. SUMMARY OF CONCLUSIONS AND RECOMMENDATIONS

We have correlated structural effects in LC ester mixtures with properties of  $\sigma_{\parallel}/\sigma_{\perp}$ ,  $\Delta\epsilon$ ,  $\Delta n$ , and  $\eta$  for favorable DS characteristics. Five out of eight classes of LC ester structures tested in mixtures were found to be thermally stable at elevated temperatures when in the absence of oxygen, even with redox dopants added. Although three LC ester mixtures showed generally favorable DS properties at elevated temperatures, only one of our mixtures had both high and low temperature stability. It had a relatively high  $V_{th}$  due to cybotactic nematic characteristics. While the three mixtures are quite thermally stable as evacuated samples, they showed severe thermal degradation as thin layers in unsealed glass cells when traces of oxygen were present. They showed fairly good thermal stability in their evacuated cells, but severe electrochemical degradation occurred in cells made with epoxy sealants due to conductive impurities picked up from the sealant at elevated temperatures.

It is of primary importance to identify the cause of the surface-catalyzed thermal degradations of LC ester mixtures in glass cells and to determine how the reactions depend upon surface properties and traces of oxygen. The reaction products and mechanisms need to be established first with relatively simple mixtures, followed by studies of corrective measures to passivate the surfaces. Sealant materials and techniques must be studied to find ways to minimize the contamination of the LCs with conductive impurities that are harmful in the dc activation of displays. Mixtures with revised LC components need to be evaluated for lower viscosity, faster dynamic scattering response times, and lower threshold voltages as well as stability at high and low temperatures. New redox dopant structures should be evaluated in LCs to obtain decreased sensitivity to oxygen and to improve the dc dynamic scattering characteristics.

## SECTION 2

### RESEARCH RESULTS

Most of our results are described in Appendix A, "Ester Liquid Crystal Mixtures For Dynamic Scattering at Elevated Temperatures," which is a paper that has been submitted for publication in Molecular Crystals and Liquid Crystals. In this section we will comment on highlights of the results presented in Appendix A, and we describe some other results which are not included in that paper.

#### A. LC EUTECTIC MIXTURES AND THEIR CHARACTERISTICS

Six eutectic nematic mixtures are used with clearpoints in the range of 72° to 81°C. Structural effects are evaluated by using different combinations of components from eight classes of esters, including phenyl benzoates, phenyl thiobenzoates, phenyl cyclohexanecarboxylates, phenyl acyloxybenzoates, as well as a phenyl benzoyloxybenzoate and a phenyl biphenylcarboxylate structure. The structural classes are shown in Figure A-1.\* The composition and properties of the mixtures are shown in Tables A-I, A-II and A-III,\* along with the HRL abbreviations for the components and the mixtures. After long periods of cooling at -40°C, two of the mixtures (HRL-26N3, and -256N5) completely remelt well below 0°C while two of them (HRL-25N4, and -2N52) melt near 6°C. However, the other two (HRL-246N1 and -26N4) melt near 20°C, which is considerably higher than their calculated eutectic values. The actual eutectic composition of the latter two mixtures is probably different than that calculated. Such deviations appear to be due mainly to the acyloxybenzoate and the biphenylcarboxylate ester components.

Comparisons of the  $\Delta n$  and  $\eta$  values of these mixtures with those of other mixtures studied recently<sup>13-15</sup> indicate that the cyclohexanecarboxylates lower both  $\Delta n$  and  $\eta$  considerably, while  $\Delta n$  is increased by the

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\*Fig. A-1 is Fig. 1 in Appendix A; Table A-1 is Table I in Appendix A; etc.

thioesters, and  $\eta$  is increased substantially by the benzoyloxybenzoate component, and especially by the *o*-cyanophenyl biphenylcarboxylate component. The effect of  $\Delta\epsilon$  on the  $V_{th}$  values of DS are plotted in Figure A-2, and show that small  $\Delta\epsilon$  values in the range -0.4 and 0.1 are best for low dc- $V_{th}$  in surface- $\pi$  cells. The dc-DS curves at room temperature are shown in Figure A-3, where the gradual increase in %S with the voltage from  $V_{th}$  to 20 V dc is a favorable condition for obtaining gray scale levels in a display. There is a general correlation of increased DS response time with increased  $\eta$  of the mixtures as shown in Figure A-4. The mixtures with the lowest viscosities (HRL-26N3 and -26N4) have the fastest DS response times.

#### B. SCATTERING ANGLE STUDIES

The relative intensity of off-normal DS as a function of angle is obtained using a well collimated green light (525 nm peak) beam of full cell size at normal incidence on the cell, and then measuring the transmitted scattering intensity at off-normal angles. The acceptance angle for receiving the scattered light is about 2° wide. A half-Lambertian scattering plate is used as a reference in place of the DS cell. A sample of *p*-methoxybenzylidene *p*-butylaniline (MBBA) doped with 0.2% tetrabutylammonium tetraphenylboride (TBATPB) is used as a reference scattering LC, while the other LC mixtures in this study all contained 0.5% redox dopant. The results are shown in Figures 1-4. It should be noted that the scattering data shown here exaggerates the relative scattering intensity at small angles. (The incident beam fills the whole cell, and the part of the beam nearer to the detector is more easily scattered into it. This is especially significant at small angles where the scattered light is most intense.) Nevertheless, the relative scattering angle properties of the mixtures compared under the same conditions are shown in Figures 1-4. Of the six ester mixtures, HRL-26N3 has the best small angle scattering, up to about 6° off normal, but has the poorest wide angle scattering in the above 11°. On

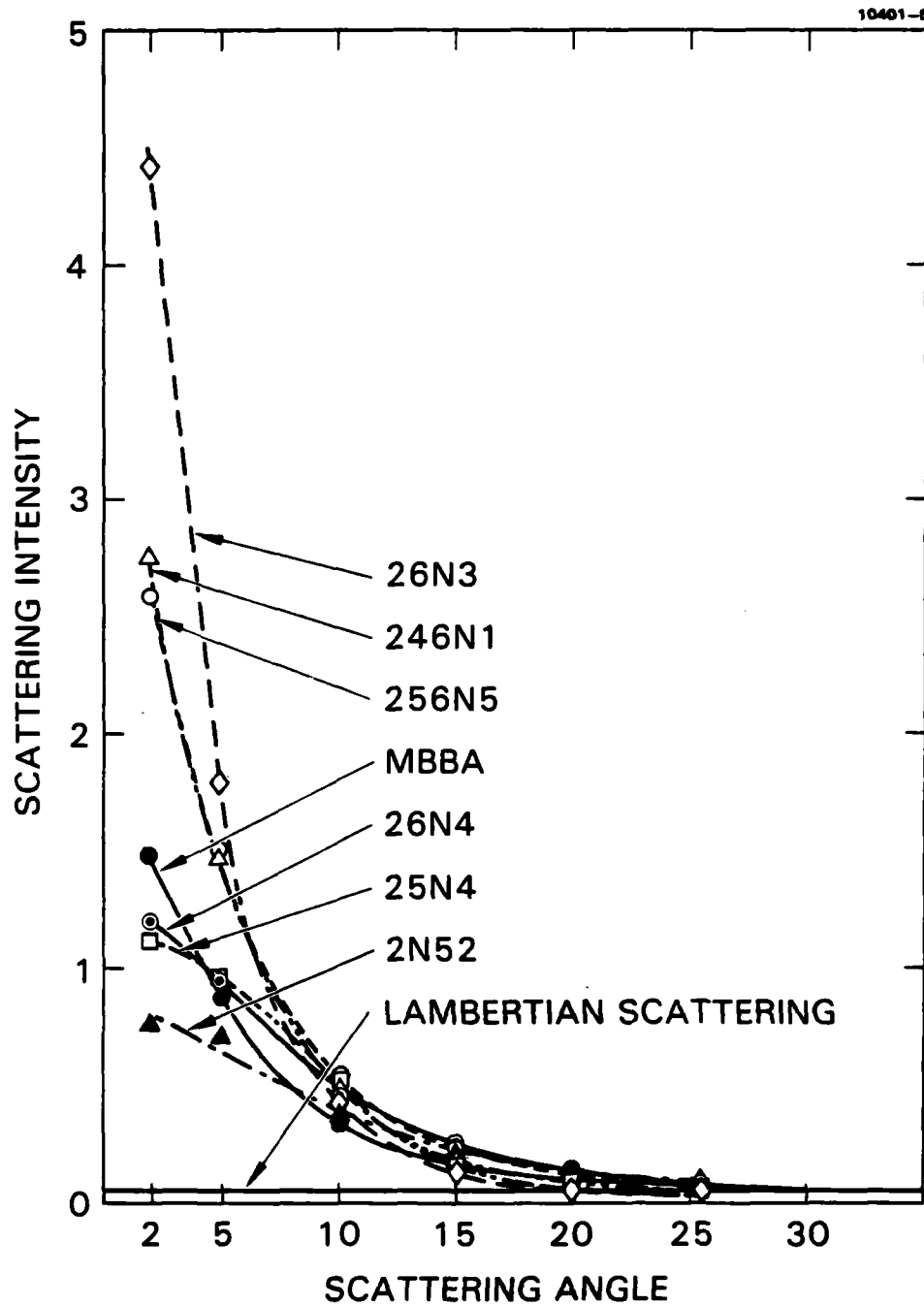


Figure 1. Relative scattering intensity of mixtures at off-normal angles from DS at 20 V dc. (0.5% DBF/TFM, 8.4  $\mu$ m cell, 23°C, surface-II).



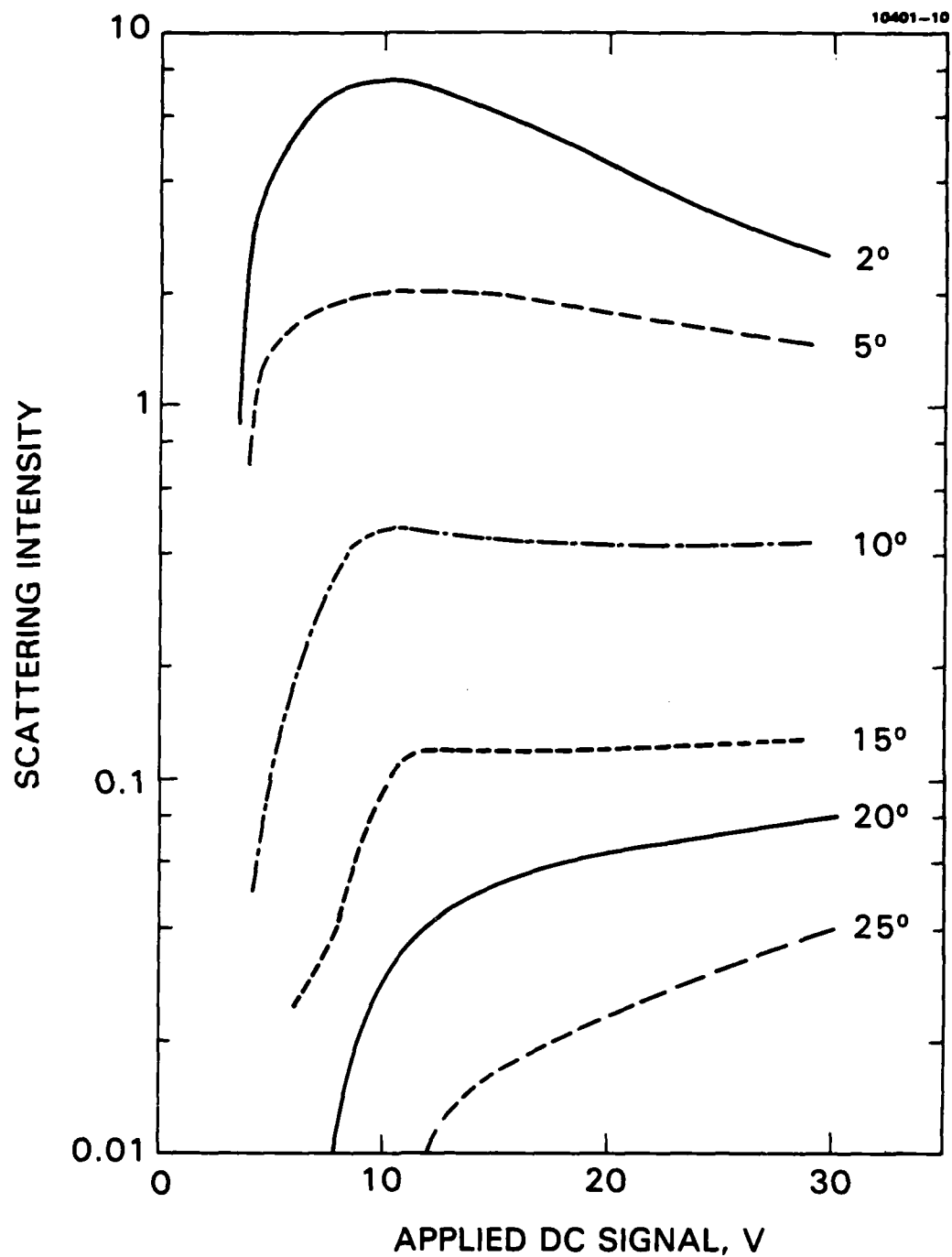


Figure 2. Relative scattering intensity of HRL-26N3 as a function of voltage and scattering angle. (0.5% DBF/TFM, 8.4  $\mu\text{m}$  cell, surface- $\parallel$  23°C.)

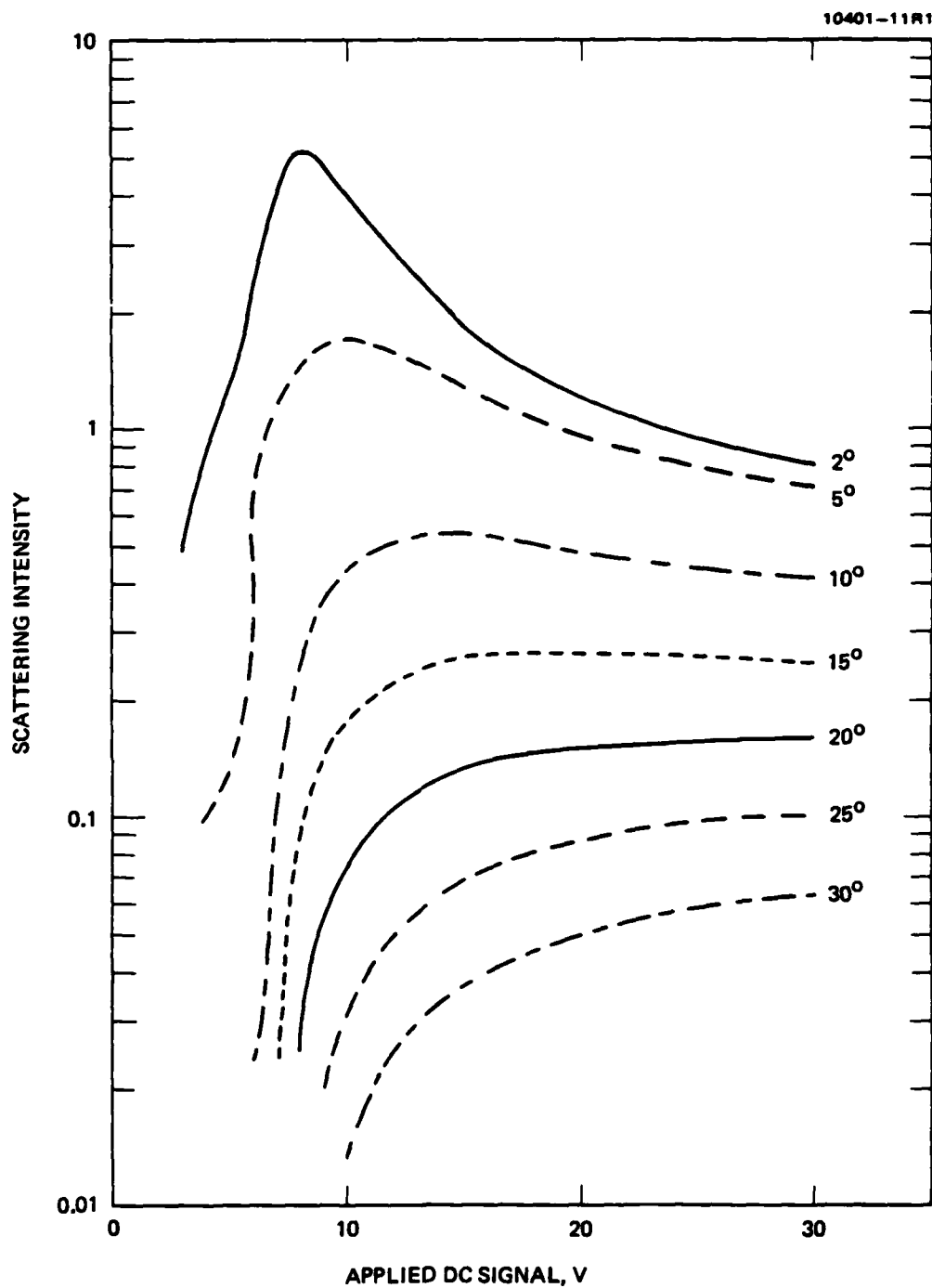


Figure 3. Relative scattering intensity of HRL-26N4 as a function of voltage and scattering angle. (0.5% DBF/TFM, 8.4  $\mu\text{m}$  cell, surface- $\parallel$ , 23°C.)

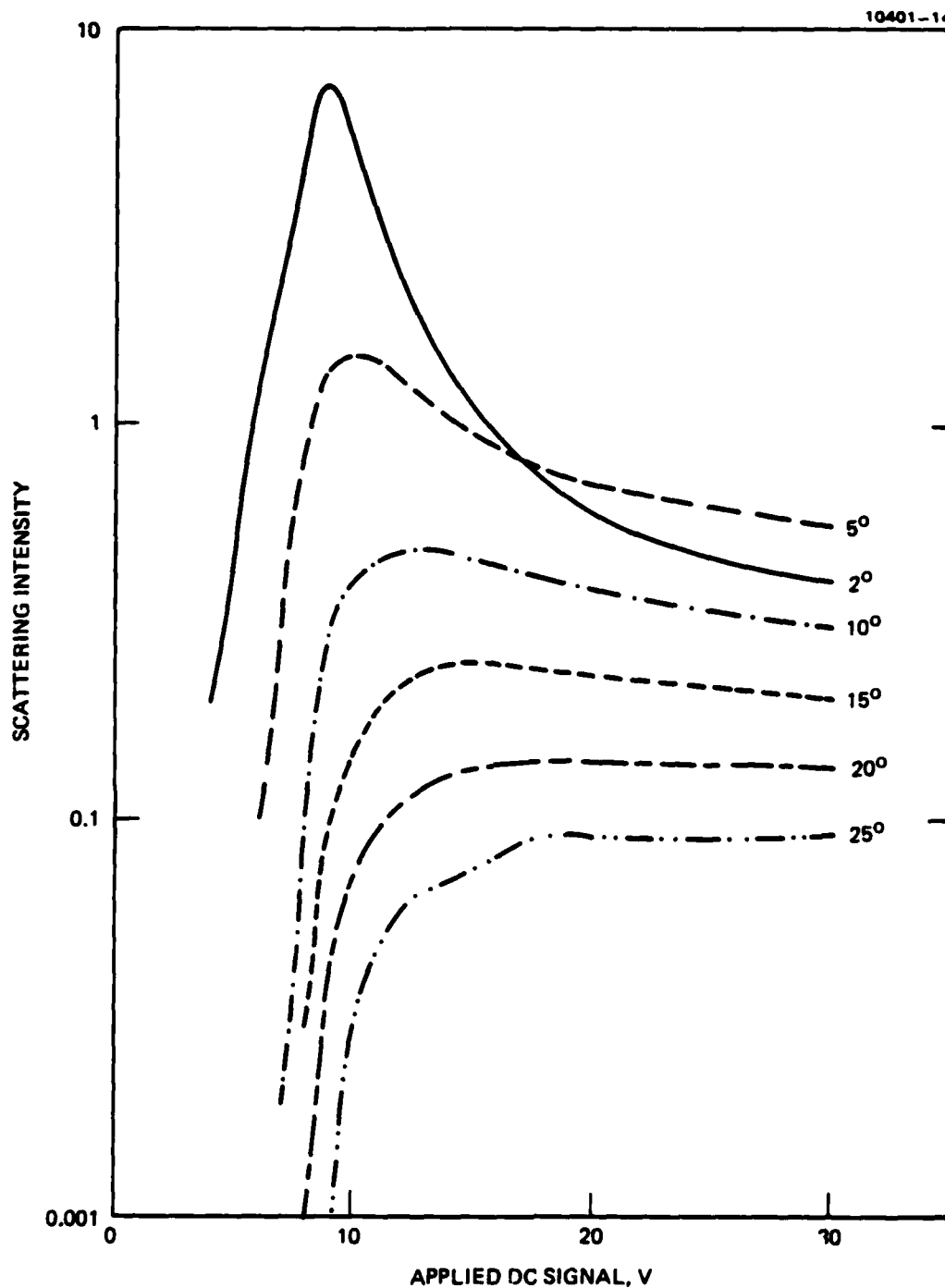


Figure 4. Relative scattering intensity of HRL-2N52 as a function of voltage and scattering angle. (0.5% DBF/TFM, 8.4  $\mu\text{m}$  cell, surface-II, 23°C.)

the other hand, HRL-2N52 has the poorest small angle scattering, and the best wide angle scattering above  $20^\circ$  off-normal. We find no obvious relationship of birefringence or other properties with the scattering angle characteristics of these mixtures. Several of these ester mixtures have better scattering properties (at both small and large angles) than does TBATPB-doped MBBA, which is shown as a reference curve in Figure 1. More complete data on the scattering angles of HRL-26N3 -26N4, and -25N2 are shown in Figures 2-4. In general, the region in which the scattering increases with increased voltage occurs at lower voltages for small angles, and at higher voltages for wide angles. For example, HRL-26N3 shows a linear increase of scattering with voltage in the 2 to 10V range at  $2^\circ$ , and in the 12 to 30V range at  $25^\circ$ . These data indicate that at higher voltages a display might show inverse images at small scattering angles. The scattering effects need to be studied with an improved scattering apparatus, and with signal pulses of the type generated in a matrix display.

#### C. LC PROPERTIES AT ELEVATED TEMPERATURES

The effect of elevated temperature on the  $n$ ,  $\Delta\epsilon$ ,  $\epsilon$ ,  $\sigma_{\parallel}/\sigma_{\perp}$ , and  $\rho_{ac}$  of the mixtures are shown in Figures A-5 through A-9, and are discussed in Appendix A. One of the most interesting effects is that the mixtures show evidence of cybotactic nematic character (short range smectic order) at lower temperatures, as indicated by the increase of  $\sigma_{\parallel}/\sigma_{\perp}$  with increasing temperature to give a maximum  $\sigma_{\parallel}/\sigma_{\perp}$  value. The cybotactic nematic effect is most evident in HRL-26N3, where it causes lower  $\sigma_{\parallel}/\sigma_{\perp}$  values, which in turn are responsible for its relatively higher  $V_{th}$  values in surface- $\pi$  cells. Thus, a revised composition in which the cybotactic nematic character of HRL-26N3 is decreased should further improve its scattering efficiency by increasing its conductivity anisotropy.

The  $\rho_{ac}$  of the mixtures changes by about an order of magnitude in the  $45^\circ$  range, between  $25^\circ$  and  $70^\circ\text{C}$ , as shown in Figure A-9. Slightly

steeper plots of this type are obtained for the apparent dc-resistivity of these mixtures in surface- $\mu$  cells when DS is activated with 20 V dc. In HRL-26N3 the apparent  $\rho_{dc}$  changes by an order of magnitude in the 36° range, between 35° and 71°C, as shown in Figure 5. (although the samples in Figure 5 are slightly contaminated by sealant impurities, the results are usable since the same relative changes in  $\rho_{dc}$  at 20 V dc are observed in unsealed heated cells.) Similarly, an order of magnitude change in  $\rho_{dc}$  is shown (Figure 5) in the 33° to 71° range for HRL-26N4, and in the 29° to 71° range for HRL-2N52. If parallel changes occur at lower dopant concentrations, then these correspond to the temperature ranges in which the LC samples can be operated in a matrix display with  $\rho_{dc}$  maintained between  $10^9$  and  $10^{10}$  ohm-cm. This is the approximate  $\rho_{dc}$  range required in a matrix display, so that at 71°C the charge on each pixel capacitor does not leak off too fast in a 1/30 sec frame time (i.e.  $\rho_{dc} > 10^9$  ohm-cm), and so that at 35°C the LC is conductive enough to show good DS (i.e.,  $\rho_{dc} < 10^{10}$  ohm-cm).

#### D. DYNAMIC SCATTERING AT ELEVATED TEMPERATURES

The dc-DS curves of scattering versus voltage (Figures A-10 and A-11) show improved DS with increasing temperature in the range between  $V_{th}$  and about 10 V dc, as discussed in Appendix A. However, the mixtures show some fall-off in scattering efficiency between 10 and 20 V dc, especially at the higher temperatures (e.g., above 60°). This may be partly due to the decrease in clearpoint of the mixtures in the presence of added redox dopants (as shown in Table A-IV). Thus, it appears desirable to modify the LC and/or dopant compositions so that revised LCs have clearpoints above 75°C, even after doping.

DC-activated dynamic-scattering curves and response times are studied with the more stable redox-doped mixtures. The effects of temperature on threshold voltage, scattering level at 15 to 20 V, transmission contrast ratio, and response time are examined. All measurements

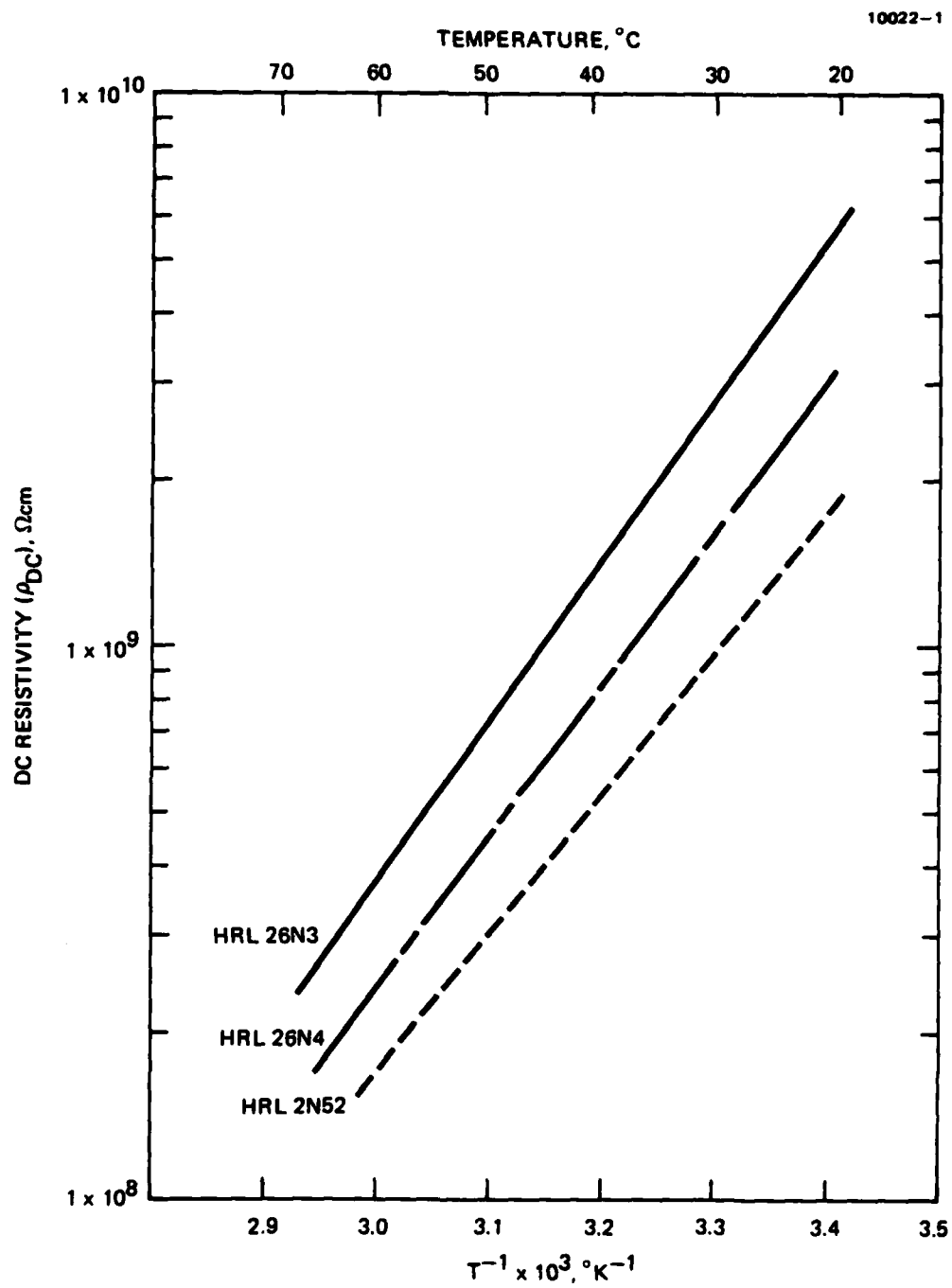


Figure 5. Qualitative effect of temperature on dc resistivity of redox-doped LCs.

are taken in transmission with normal incidence of light, in sealed cells with nominal 13 $\mu$ m-thick spacers. The cells are vacuum filled and have surface-parallel alignment on ITO electrodes. A typical set of scattering curves is shown in Figure 6 with 0.5% redox dopant in HRL-26N3 at temperatures between 23° and 63°C. Although the effect is not always large, it can be seen in Figure 6 that the threshold ( $V_{th}$ ) is lower at higher temperatures. Compared to room temperature, the scattering levels are higher at high temperatures in the region of about 5 to 12 V, but are lower at higher temperatures above 15 V. In general, there should be a slight advantage to having this type of temperature dependence on  $V_{th}$  and scattering in warm matrix cells where the voltage from a pixel element decreases during a frame time, because the charge leaking through the LC increases with increasing temperature.

All three of the thermally stable mixtures have good scattering efficiencies in the 15- to 20-V range, as shown in Table 1. The transmission contrast ratios at 15 and 20 V show small temperature variations. However, the lowest contrast ratio measured, ~17:1, at 68°C, is still above the 15:1 specification for the matrix display. Although there is undoubtedly some conductivity contamination from the sealant, these results are probably not seriously affected by these heating times, as found by the reproducibility of results at 23°C before and after heating.

Elevated temperatures significantly decrease the DS response times, as shown by the  $T^{-1}$  plot in Figure A-12 for 15 V dc activation in cells with a 8.4  $\mu$ m thickness of LC. For additional comparisons, plots of response times (log scale) versus °C are shown for 20 V dc activation Figure 7. The ratio of  $\tau_D/\tau_{on}$  is more favorable at 20 V than at 15 V dc, since at higher voltage  $\tau_D$  increases, and  $\tau_{on}$  decreases. For example, at 20 V and 64°C the  $\tau_D/\tau_{on}$  values are 84 ms/4 ms for HRL-2N52, and are 80 ms/7 ms for HRL-26N3. Thus, at elevated temperatures the use of higher voltages favors the TV display condition of:  $\tau_{on} < \text{frame time} < \tau_D$ . There is also an advantage in having  $\tau_{on} \ll \text{frame time}$  at elevated temperatures, because the LC pixel element can be fully activated,

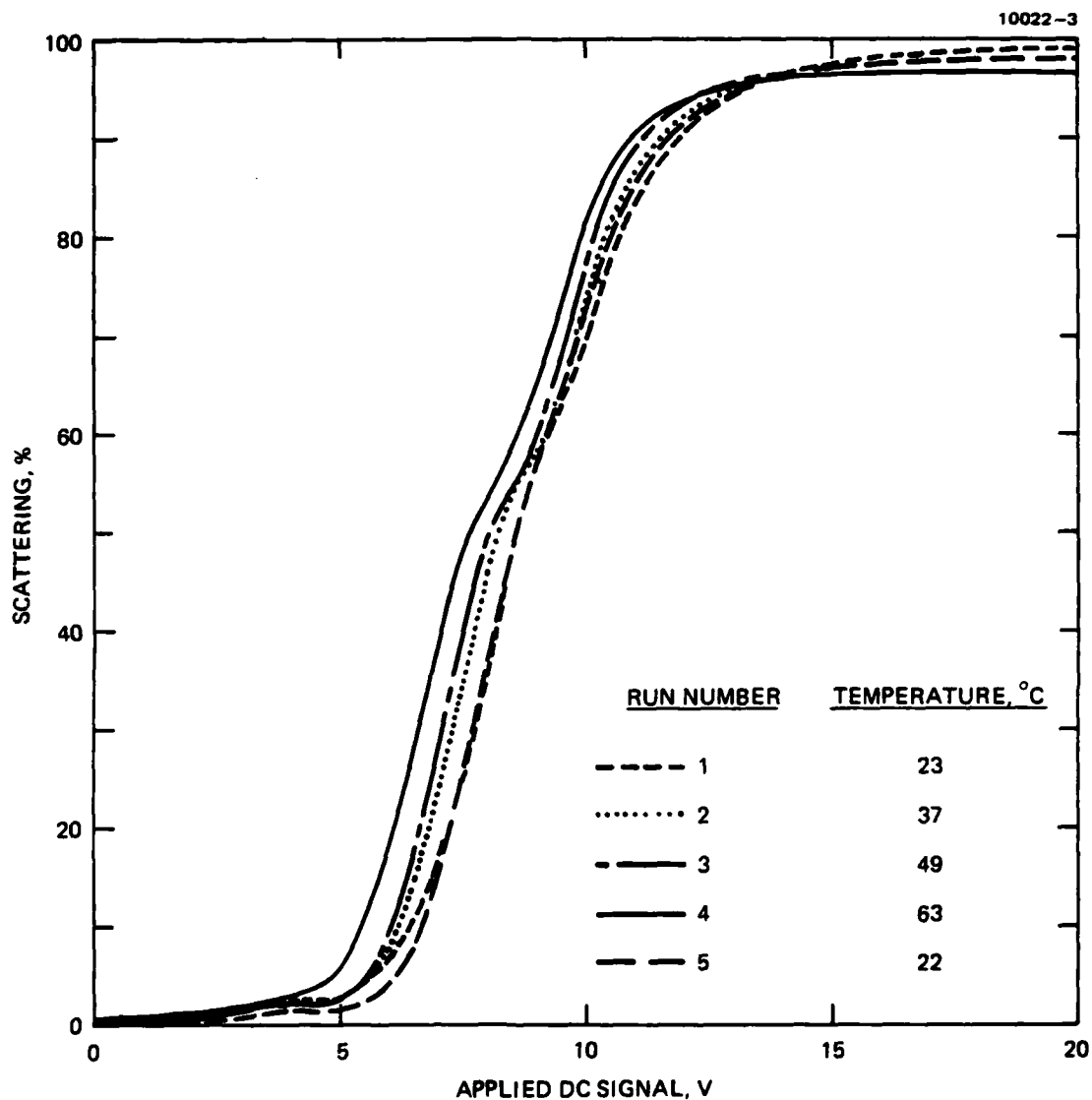


Figure 6. Effect of temperature on dc-activated dynamic scattering of HRL-26N3 with 0.5% redox dopant. (Surface-II, sealed cells, nominal 13- $\mu$ m spaces, transmission measurements.)



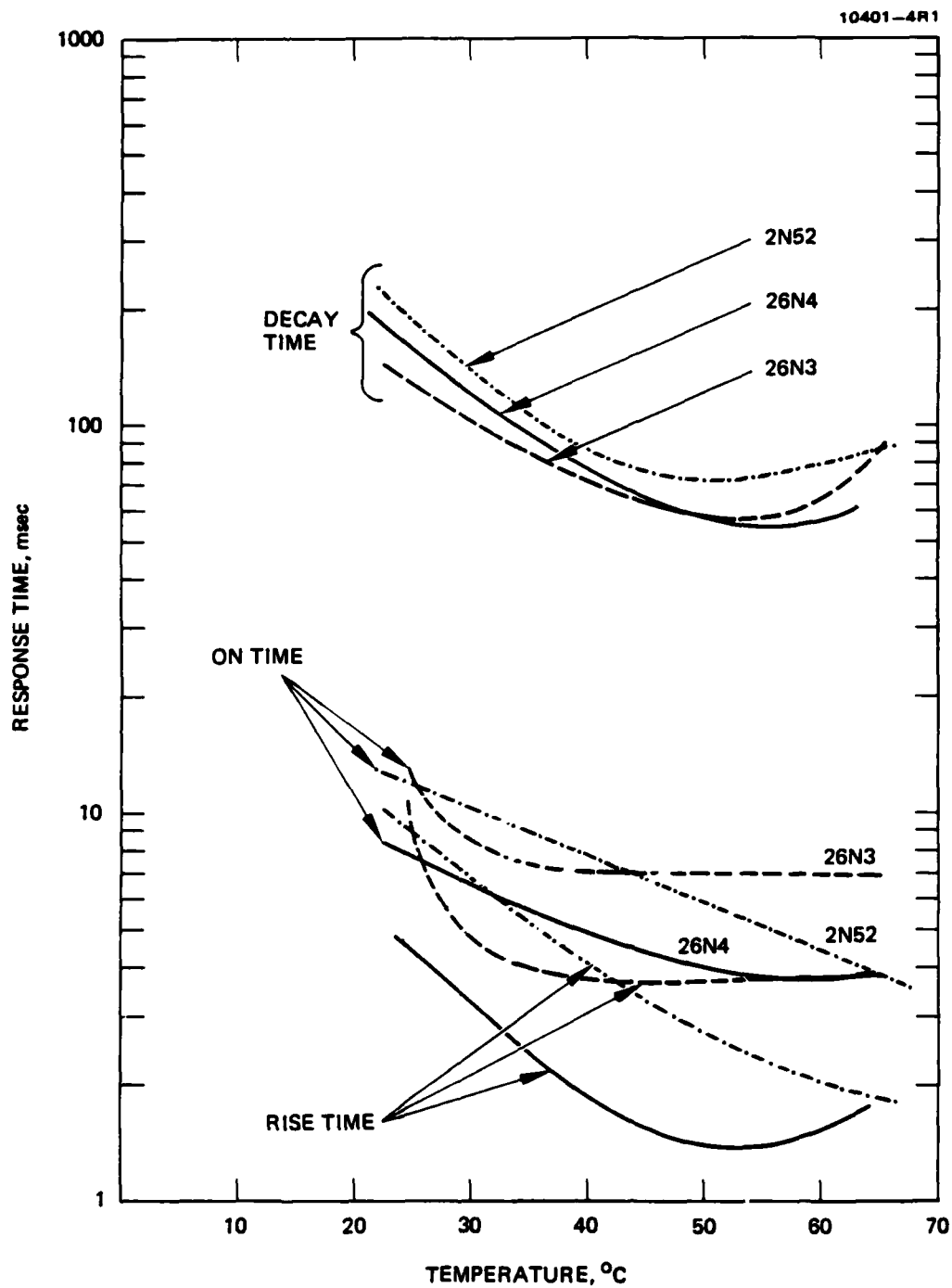


Figure 7. Effect of temperature on dc-DS response times from 20 V dc. (0.5% DBF/TFM, 8.4  $\mu$ m thickness cell, surface- $\parallel$ .)

Table 1. Effect of Temperature on Dynamic-Scattering Characteristics

LC HRL Number	Temperature, °C	Resistivity, $\Omega$ -cm	% Scattering		Contrast Ratio <sup>a</sup>	
			15 V	20 V	15 V	20 V
26N3	23	$5.77 \times 10^9$	97.4	99.0	38	99
	37	$1.73 \times 10^9$	97.0	98.0	33	49
	49	$8.33 \times 10^8$	97.1	98.0	34	50
	62	$3.23 \times 10^8$	96.5	96.5	28	28
26N4	23	$3.18 \times 10^9$	98.2	99.0	55	99
	36	$1.04 \times 10^9$	98.7	99.2	77	125
	50	$4.08 \times 10^8$	98.3	99.0	59	99
	67	$1.75 \times 10^8$	98.2	98.8	55	83
2N52	22	$1.71 \times 10^9$	98.7	99.1	77	111
	34	$6.94 \times 10^8$	98.6	99.0	70	99
	42	$4.61 \times 10^8$	98.8	99.2	82	124
	54	$2.05 \times 10^8$	98.5	99.0	66	99
	68	$1.29 \times 10^8$	96.2	94.2	26	17
<sup>a</sup> Contrast ratio at 15 V = $\frac{\text{Transmission at 15 V}}{\text{Transmission at } V_{th}}$						

even at relatively low resistivities ( $< 10^9$  ohm-cm) if  $\tau_{on}$  is less than the time of the charge decay of the pixel capacitor. This, in turn, would permit use of higher dopant concentrations, and would extend the useful temperature range of a matrix display. Thus, it may be possible to develop LCs capable of being operated from 25° to 71°C in a matrix display.

#### E. THERMAL STABILITY AT ELEVATED TEMPERATURES

Many of our thermal stability tests are summarized in Table A-IV, which shows results from heating samples at an accelerated condition of 100°C. Four of the mixtures show excellent stability when heated for 2500 hrs at 100°C as bulk samples in evacuated glass test tubes, after first degassing them on a vacuum line with a freeze/thaw technique. The other two mixtures (HRL-25N4 and HRL 246N1) show no significant change in clearpoint, but show a small increase in conductivity and slight yellow coloration in the evacuated tubes. The high performance liquid chromatography analysis of HRL-256N5 is shown in Table 2 for samples before and after heating in evacuated glass tubes. The peak positions (retention times) and the relative peak heights (measured at 254 nm) are not significantly changed by this heating experiment.

The results in Table A-IV indicate fairly good stability for all of the mixtures after heating for 3200 hr at 100°C in crimp-sealed Al DSC pans. There was no change in clearpoint. But after removal from the pans, the samples showed substantial decreases in resistivity, and enough conductive species was present to produce dc-DS in four of the mixtures. This indicates probable thermal sensitivity to oxygen, since the DSC pans were not evacuated. The decreased  $\rho$  could be a serious problem if the ionic species thus generated interferes with the electrochemical reversibility of the LCs when redox dopants are present. Liquid chromatography analysis of HRL-25N4 and HRL-256N5 before and after the prolonged heating in DSC pans are shown in Table 3. The peak heights are nearly the same, within experimental error. But the heated samples do show some increases in impurity peaks.

Table 2. Thermal Stability Studies of HRL-256N5

Liquid Chromatographic Separation of 256N5 LC with Solvent Mixture  
Hexane: Chloroform: Acetonitrile (72:1:1)

Components	Starting Material		Heated in Evac. Tube <sup>(a)</sup>	
	Retention Time Min	% Peak Height	Retention Time Min	% Peak Height
I <sup>(b)</sup>	5.55	$3 \times 10^{-3}$	5.55	$1 \times 10^{-3}$
20-(C)3	7.01	0.7	7.01	0.6
20-5	7.80	6.1	7.83	6.5
20-3	8.39	24.1	8.46	25.5
1065				
40-05	8.86	25.8	8.90	27.4
60-01	12.20	11.6	12.44	10.5
10606	12.76	19.8	13.07	18.8
60-00C5	13.66	4.5	14.37	4.4
I <sup>(b)</sup>	15.75	$1 \times 10^{-2}$	15.59	$2 \times 10^{-2}$
40-00C4	16.34	5.9	16.42	4.6
I <sup>(b)</sup>			19.06	$7 \times 10^{-3}$
I <sup>(b)</sup>	20.63	$2 \times 10^{-2}$	20.91	$2 \times 10^{-2}$
10-00C3	31.02	1.6	31.73	1.7
<p>(a) 2000 hours at 100°C.</p> <p>(b) I = Impurity.</p>				

Poor stability was found when heating the mixtures (1980 hr at 100°C) as thin LC layers (13  $\mu$ m thick) in unsealed test cells with FG/ITO/IBE\* glass substrates. Even though heated in a N<sub>2</sub>-flushed oven, all of the unsealed cells showed decomposition in the form of some high melting crystalline products in the LCs, as indicated in Table A-IV. The crystals must be reaction products because they all melt at higher than the mp of any of the initial components. Some of the products are probably also LCs, since the clearpoint of the remaining LC fluid is increased in each mixture. Liquid chromatography analysis of LC samples from the unsealed ITO cells are shown in Tables 3 and 4. Results indicate that in these cells there is substantial loss of the lower molecular weight LC components, especially 20-[C]3, 20-3 and 20-5. Some of the peaks increase in size, such as those at the retention times of 40-05, 60-00C5, and 10S06. These increases are probably due to the formation of products which are not resolved in retention time from the starting materials. Analysis of samples of HRL-256N5 heated in a vial open to air are also shown in Tables 3 and 4. Comparisons with the starting material, and with the unsealed ITO cells, show that the LC from the open vial changes less in its relative peak heights than the LC from the unsealed cells. (However, there may be oxidation products from the vial experiment that are too polar to come off the column.) Many impurity peaks are observed in the LC heated in the open vial that are at the same retention times as occur in the LC heated in the unsealed cells. Our conclusion that traces of oxygen are involved in the degradation mechanism is consistent with this observation.

No crystal formation is observed in thin layer test cells, which are evacuated and sealed, as indicated in Table A-IV, for three of the mixtures heated 2820 hr at 100°C. However, the  $\rho$  of the LCs decreases substantially due to contaminants from the epoxy sealant. These ionic impurities do not provide good electrochemical stability to the LC, as found by rapid degradation of the undoped LC in the sealed cells as 20 V dc and 55°C after their long period of heating at 100°C. Other

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\*FG/ITO/IBE refers to float glass with indium tin oxide conductive glass that is ion-beam-etched for alignment, as indicated in Appendix A.

Table 3. Thermal Instability Effects

Liquid Chromatographic Separation with Solvent Mixture Hexane:  
Ethylacetate (98:2)

Components	Retention Time, Minutes	% Peak Height						
		25 N4			256N5			
		Initial	DSC Pan (a)	ITO Cell (b)	Initial	DSC Pan (a)	ITO Cell (b)	Vial (c)
I <sup>(d)</sup>	2.80	$3 \times 10^{-2}$	$3 \times 10^{-2}$	$4 \times 10^{-2}$	—	—	—	—
60-5	3.07	28.3	28.5	38.1	—	—	—	0.2
I	4.45	$2 \times 10^{-3}$	$1 \times 10^{-2}$	$2 \times 10^{-3}$	—	—	—	—
20- (C) 3+20-5	4.80	6.3	6.3	1.7	8.2	7.9	3.4	8.3
20-3	5.24	5.1	5.2	0.1	6.9	6.5	0.5	6.4
10-5	5.91	23.2	22.9	15.8	29.1	28.8	23.2	32.2
40-05	6.50	17.2	17.2	22.9	23.5	24.8	32.9	25.3
I	8.42	$2 \times 10^{-2}$	$2 \times 10^{-2}$	0.1	—	0.4	1.2	1.4
60-00C5	10.08	—	—	—	6.4	5.6	7.4	0.8
60-01	10.51	12.4	12.3	12.0	16.0	16.3	18.5	17.2
10-06	11.26	4.9	4.9	6.8	6.6	6.7	9.8	7.5
10-04	12.87	2.6	2.6	2.5	—	—	—	
40-00C4	12.60	—	—	—	2.2	1.9	1.7	
I	14.29	—	$8 \times 10^{-3}$	$2 \times 10^{-3}$	—	—	0.2	$2 \times 10^{-2}$
I	18.74	$3 \times 10^{-3}$	$8 \times 10^{-3}$	$1 \times 10^{-2}$	—	—	0.2	$4 \times 10^{-2}$
I	21.65	$7 \times 10^{-5}$	$3 \times 10^{-2}$	$3 \times 10^{-2}$	—	—	0.3	—
10-00C3	26.34	—	—	—	1.0	0.7	0.3	$1 \times 10^{-2}$

(a) LC mixtures heated in sealed Aluminum pans (DSC) for 3200 hours at 100°C.

(b) LC mixtures heated in unsealed IBE ITO cells (N<sub>2</sub> flushed oven) for 2000 hours at 100°C.

(c) LC mixture heated in glass vial open to air for 1180 hours at 100°C.

(d) I = Impurities.

Table 4. Thermal Instability Effects in HRL 256N5

Liquid Chromatographic Separation with Solvent Mixture Hexane:  
Ethylacetate (98:2)

Components	Starting Material		Unsealed to ITO Cell Heated in N <sub>2</sub> <sup>(a)</sup>		Open Tube Heated <sup>(b)</sup> In Air	
	RT <sup>(c)</sup> , Min	% PH <sup>(d)</sup>	RT, min	% PH	RT, Min	% PH
I <sup>(e)</sup>			3.15	>0.28	3.07	0.16
I					3.43	0.07
20-5+20-(C)3	4.72	8.16	4.76	2.54	4.76	8.33
20-3	5.16	6.52	5.20	0.10	5.16	6.38
1055	5.87	28.66	5.83	20.13	5.87	32.20
40-05	6.30	24.47	6.34	34.94	6.30	25.26
I	8.19	0.03	8.19	1.39	8.19	1.39
60-00C5	9.69	6.52	9.76	8.80	9.53	0.83
60-01	10.28	15.85	10.39	18.28	10.47	17.21
10506	10.98	6.75	11.10	10.88	11.14	7.50
40-00C4	12.13	2.10	12.20	2.32	12.20	
I			13.94	0.17	13.82	0.02
I			17.17	>0.28	17.05	>0.35
I			18.31	0.14	18.31	>0.35
I			20.00	0.02	19.92	0.04
I	21.02	0.01	20.87	>0.28	21.30	>0.35
I			22.68	0.07		
10-00C3	25.00	0.93	25.47	0.19	25.39	0.01
I					28.50	0.02
I					32.44	0.05
I			38.19	0.03	37.28	0.28
I					40.51	0.10
I					43.19	0.10
I					82.17	0.05

(a) Heated for 2000 hrs at 100°C.

(b) Heated for 1180 hrs at 100°C.

(c) Retention time in minutes.

(d) Peak height, show as % of total sum.

(e) I = Impurity

qualitative tests show that crystalline products are not formed in heated evacuated tubes with water added. But they are formed rapidly in unsealed cells made up on glass substrates (no ITO) heated at 100°C in a N<sub>2</sub>-flushed oven.

#### F. THERMAL STABILITY OF REDOX-DOPED MIXTURES

Studies of the thermal stability of the LC mixtures with redox dopants (DBF and TFM) added are also shown in Table A-IV. Evacuated tubes containing 1% of the redox dopants were heated for 2300 hr at 100°C. The results indicate that the mixtures having fairly good thermal stability with the redox dopants are HRL-26N3, -26N4, and -2N52. (The stability of HRL-2N52 is implied on the basis of common components with the others, and has been confirmed by other tests.) The HRL-25N4 mixture contains the most thioester components, and reacts most strongly with the redox dopants at 100°C. HRL-256N5 also contains a thioester and shows some reaction. The reactivity of the HRL-246N1 mixture with the redox dopant is believed to be due to its biphenyl component, which is the only ester class in HRL-246N1 that is not in HRL-26N3 and -26N4. A well-sealed test cell (FG/ITO/PVA substrates, sealed with Type II Ablefilm 539, and evacuated) containing a 13 µm thickness of HRL-2N52 with 0.25% redox dopant showed no crystals or discoloration after 5430 hrs of heating at 100°C. Collectively, these results indicate that five of the eight classes of LC esters in Figure A-1 have good thermal stability, even in the presence of the redox dopant.

#### G. ELECTROCHEMICAL STABILITY AT ELEVATED TEMPERATURES

While we previously have successfully operated redox-doped LC sealed cells (made with Ablefilm 539) for long periods at 20 V dc at room temperature, we find that they can be operated only for a few days at 55°C before material deposits on the ITO electrodes. This problem arises because the sealant introduces ionic impurities that cause electrochemical degradation even in undoped LCs. Thus, we have



tested the electrochemical stability of unsealed cells at 55°C in a N<sub>2</sub>-flushed oven, even though we know that some thermal instability can be expected to occur gradually in these unsealed cells. Typical results are shown in Figure A-15 for our three most thermally stable LC/redox mixtures, with a range of DBF/TFM concentrations, and with reflective as well as transmission-type cells. No serious defects appeared in any of the cells until after 1500 hrs of 20 V dc at 55°C. More stable resistivity values were observed in the two cells with reflective Ag electrodes, one of which contained HRL-2N52 and the other HRL-26N4. In general, the electrochemical stability of the three more thermally stable mixtures with redox dopants appears to be fairly good at 55°C, and probably would be much better in evacuated cells made with a non-contaminating sealant.

### SECTION 3

#### CONCLUSIONS AND RECOMMENDATIONS

We have shown that wide-temperature-range nematic eutectic mixtures of esters can be used for dc-DS, including mixtures containing esters of the same molecular length, but from different classes of structures. In general, low  $V_{th}$  for dc-DS is favored by high values of conductivity anisotropy, and small (near zero) values of dielectric anisotropy in cells with surface- $\pi$  alignment. Both the on-time and the decay time of DS are generally faster in the lower viscosity mixtures. Among the eight ester classes studied (see Figure A-1) in six mixtures, the RO-[C]R', and RO $\phi$ R' structures have relatively low viscosity, while the R(CN)- $\phi$ R' and R-(Cl)OOC $\phi$ R' structures have relatively high viscosity. New mixtures with lower viscosities could be prepared by optimizing such structural factors. The mixture with the best low temperature stability is HRL-26N3; without dopant added it has a nematic range of -20° to 76°. It also has the lowest viscosity; fastest DS time responses, and best small angle scattering of the six mixtures. However, its  $V_{th}$  is somewhat high because cybotactic nematic effects decrease its conductivity anisotropy. Revised compositions would be advantageous if they decrease the cybotactic nematic character and viscosity compared to HRL-26N3, but retain its thermal stability and the wide nematic range characteristics.

The addition of the DBF/TFM redox dopants lowers the clearpoint of the LC mixtures by a few degrees. Thus, it would be advantageous to devise revised mixtures with clearpoints above 80°C without dopant added so that they would have an adequate order parameter at the maximum operating temperature of 71°C. Some of the dc-DS characteristics improve at elevated temperatures, notably the  $V_{th}$  decreases, and the  $\tau_{on}$  becomes short compared to the typical 33 ms frame time of a matrix display. The temperature dependence of  $\rho_{dc}$  is such that it changes approximately an order of magnitude between 35° and 71°C. New mixtures

with lower viscosity would be expected to result in shorter DS turn-on times, which might permit use of somewhat more conductive LCs (i.e., more dopants added) in matrix cells at elevated temperatures if  $\tau_{on} \ll$  frame time. Thus, a lower viscosity may permit use of a lower  $\rho_{dc}$  at high temperatures, which in turn could widen the effective operating temperature range of matrix display cells.

Good thermal stability at 100°C, in the presence of the DBF/TFM redox dopants, is shown in evacuated tubes for three mixtures, which include five different classes of esters. Structures having lower stability with redox dopants are the ROSR' and ROSOR' thioesters, and the R(CN)- $\phi$ R' biphenylcarboxylate ester. However, accelerated tests at 100°C show that all the LC mixtures in unsealed test cells are thermally decomposed by traces of oxygen, and that this instability is catalyzed by glass surfaces. The general mechanism of this thermal instability needs to be determined in order to minimize the effect by passivation of the glass surfaces. This thermal degradation (in which higher melting crystals are formed) is avoided in evacuated test cells made with an epoxy film sealant. However, elevated temperatures generate conductivity impurities in the LC from epoxy sealants. These impurities greatly reduce the dc-DS lifetime of the redox-doped mixtures at elevated temperatures, indicating that improved sealants are needed. Relatively good dc-DS operating lifetime is demonstrated at elevated temperatures (>1500 hrs at 20 V dc and 55°C) in unsealed cells, with both transparent and reflective electrodes. These results indicate that the goal of stable dc-DS at elevated temperature should be reached by using LC mixtures from the five classes of esters that are thermally stable, by using redox dopants, by learning to passivate the glass substrate surfaces, and by using evacuated cells with sealants that do not introduce conductivity impurities into the LC mixtures.

## SECTION 4

### RESEARCH PERSONNEL

The following research personnel participated in these studies.

Dr. J. David Margerum, Senior Scientist.....Principal Investigator  
Mrs. Anna M. Lackner, Member Technical Staff.....Project Leader  
Dr. Siu-May Wong, Consultant  
Mr. John E. Jensen, Member Technical Staff  
Mr. Willis H. Smith, Research Assistant Senior  
Mrs. Camille I. van Ast, Research Assistant Senior

## SECTION 5

### PRESENTATIONS AND PUBLICATIONS

1. "Molecular Effects on the Properties and Dynamic Scattering of Ester Mixtures," J.D. Margerum, presented as an invited lecture at the Gordon Research Conference on Liquid Crystals, Santa Barbara, Barbara, CA, January 9, 1980.
2. "Structural Effects on Nematic Ester Mixtures and their Dynamic Scattering," J.D. Margerum, presented as an invited lecture at the liquid Crystal workshop, Japan Society for the Promotion of Science, Tokyo, Japan, July 7, 1980.
3. J.D. Margerum and A.M. Lackner. "Ester Liquid Crystal Mixtures For Dynamic Scattering at Elevated Temperatures," submitted for publication in Molecules Crystals Liquid Crystals.

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APPENDIX A

ESTER LIQUID CRYSTAL MIXTURES FOR  
DYNAMIC SCATTERING AT ELEVATED TEMPERATURES



ESTER LIQUID CRYSTAL MIXTURES  
FOR DYNAMIC SCATTERING AT ELEVATED  
TEMPERATURES

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ABSTRACT

Studies are made on the effect of elevated temperature on the properties, thermal stability, and dynamic scattering (DS) of liquid crystal, ester mixtures. Six eutectic nematic mixtures are formulated with clearpoints in the range of 72° to 81°C; structural effects are evaluated by using different combinations of components from eight classes of esters, including phenyl benzoates, phenyl thiobenzoates, phenyl cyclohexanecarboxylates, phenyl acyloxybenzoates, as well as a phenyl benzoyloxybenzoate and a phenyl biphenylcarboxylate structure. The mixtures are characterized at 25°C, and their viscosity, dielectric anisotropy, conductivity anisotropy, and dc-activated DS effects are studied as a function of temperature. Thermal instabilities are studied at 100°C, with and without redox conductivity dopants. The DS stability with 20 V dc is studied at 55°C for three of the more stable mixtures, both in transparent cells and in cells with reflective metal electrodes.

## INTRODUCTION

The dynamic scattering (DS) mode<sup>1</sup> is being studied for liquid crystal (LC) applications such as flat-panel pictorial matrix displays,<sup>2-4</sup> programmable reticle devices,<sup>5,6</sup> and automobile dashboard displays.<sup>7</sup> These devices need to be capable of both storage and operation over a wide range of ambient temperatures, particularly when used for military applications or in automobiles. For example, storage temperatures from -60° to 80°C and ambient operating temperatures of -50° to 71°C are typical requirement goals for these devices. Also, the pictorial matrix displays have been developed using circuits in which the LC is activated by direct current (dc) signals. However, there is a dearth of information on the characteristics and stability of dc-DS in LCs at various temperatures. The present study has been initiated to evaluate these issues. Since it is relatively simple to quickly heat the thin LC layer in many devices, we emphasize here studies on the effects of elevated temperatures on the LC. Previous results<sup>8,9</sup> in our laboratory showed that long-period dc-DS stability was obtained at room temperature by using specially selected dopants in phenyl benzoate LC mixtures. Thus, we have chosen to study the redox dopant pair consisting of dibutylferrocene (DBF) and 2,4,7-trinitro-9-fluorenylidene malononitrile (TFM) in various ester LC mixtures. Different combinations of components from the eight classes of ester LCs shown in Figure 1 are used in six new mixtures as a means of evaluating structural effects on DS and thermal stability.

## EXPERIMENTAL

The RO-R', RO-OR', RO $\phi$ R' components are prepared by standard esterification techniques using intermediates commercially obtainable from Eastman Kodak or Aldrich Chemical. The ester synthesis, purification, and analysis techniques are carried out in the manner recently described for the RO-R' components.<sup>10</sup> The RO-[C]R' components are prepared as described recently.<sup>11</sup> The RO-OOCR' components are synthesized by first preparing the appropriate 4-acyloxybenzoyl chloride and then reacting it with an alkoxyphenol to obtain the RO-OOCR' acyloxy ester. These are purified by preparative liquid chromatography (using Waters Association's System 500 instrument) as well as by recrystallizations. The R-(Cl)OOC $\phi$ R' component is purchased from Eastman Kodak (EK 11650) and is recrystallized before use. The R(CN)- $\phi$ R' component is purchased from E. Merck (S-1014 Licristal) and is used as received. Thin-layer chromatography and liquid chromatography analyses indicate that the impurity content is less than 0.5% for each of the components. The redox dopants (DBF and TFM) were obtained commercially and were purified as in previous studies.<sup>9</sup>

The thermal analysis by differential scanning calorimetry (DSC), the molecular length (L), flow viscosity ( $\eta$ ), birefringence ( $\Delta n$ ), dielectric anisotropy ( $\Delta \epsilon$ ), resistivity ( $\rho$ ), conductivity anisotropy ( $\sigma_H/\sigma_L$ ), and the DS voltage thresholds, scattering curves, and response times are measured by techniques recently described.<sup>10,11</sup> Low temperature stability is measured by cooling LC samples in capped test tubes for extended periods (more than a month) at -40°C, then transferring the tubes to a controlled isopropanol bath at -20°C and observing the temperature at which all of the crystals melt as the bath is gradually warmed. The DS response times are measured using the LC between optical flats with SiO<sub>x</sub> pad spacers of 8.4  $\mu$ m thickness, using surface-parallel alignment obtained by rubbing polyvinyl alcohol (PVA) coatings. The PVA, which is oven-baked after being spin-coated from aqueous solution, is

estimated to be about  $500 \text{ \AA}$  thick. The unsealed cells in the  $100^\circ\text{C}$  thermal stability tests have float glass (FG) substrates coated with an indium tin oxide (ITO) transparent conductor. These are thoroughly cleaned, are ion-beam etched (IBE) for surface-|| alignment,<sup>12</sup> and are used with  $13 \text{ }\mu\text{m}$  Mylar spacers. The sealed test cells have FG/ITO/PVA substrates, are sealed using an epoxy coated Mylar film (Ablefilm 539, Type II) of  $13 \text{ }\mu\text{m}$  thickness, and are back filled with LC after evacuation. Both the unsealed and the sealed cells used in the tests of electrochemical stability at  $55^\circ\text{C}$  have FG/ITO/PVA substrates.

## RESULTS AND DISCUSSION

### LC Components and Mixtures

The estimated molecular length and the thermal properties of components used in the mixtures are shown in Table I. The melting points and the heats of fusion are used with the Schroeder-Van Laar equation to calculate the eutectic compositions of the mixtures shown in Table II, with the exception of HRL-256N5, which is a eutectic mixture that is experimentally determined. All of the mixtures contain RO-R' and RO-OR' components, but vary in their content of other components. The HRL-2N52 mixture has only RO-OOCR' acyloxy compounds added; HRL-25N4 has only thioesters added; HRL-26N3 has only RO-[C]R' components and the R-(Cl)OOC $\phi$ R' diester added; HRL-26N4 has only acyloxy and RO[C]R' components added; HRL-246N1 has only RO-[C]R' and the R(CN)- $\phi$ R' biphenyl ester added; while HRL-265N5 has thioesters, acyloxy esters, and a RO-[C]R' ester added. A unique feature of these eutectic mixtures is the inclusion of binary sets of components, which have essentially the same molecular length, but are from different classes of esters. Such binary eutectic components are 60-01 and 10S06 in HRL-25N4 and HRL-256N5; and 20-3 and 20-[C]3 in HRL-26N4 and HRL-256N5. Similarly, 60-5, 60-[C]5,

and 80-3 are combined as a tertiary mixture of this type used in HRL-26N3. The use of such binary sets is of particular value in preparing eutectic mixtures with relatively short molecular length components.

The components are chosen to give a clearpoint above 71°C and a wide nematic range, as shown by the calculated melting points and clearpoints in Table III. The observed clearpoints (which are at the low end of the clearpoint range) are about 1° to 3° lower than the calculated values. The melting points are difficult to determine because all of the mixtures tend to supercool. The observed melting points in Table III are recorded as the temperature at which the last crystals melt in a bulk sample of the mixture after an extended period at -40°C. After cooling, the HRL-26N4 and HRL-246N1 mixtures contain small amounts of crystalline material that melt near room temperature; the calculated eutectic compositions are probably somewhat different from the actual eutectics obtainable with the same components. The HRL-26N3 mixture gives the best low temperature eutectic properties, possibly because it contains neither acyloxy nor biphenyl esters.

#### Room-Temperature Properties

The calculated average molecular length of the mixtures and several of their room-temperature anisotropic properties are also shown in Table III. The birefringence of the mixtures is increased by thioester components and is decreased substantially by the RO-[C]R' cyclohexanecarboxylate components. The viscosity is strongly increased by the R(CN)- $\phi$ R' component and is greatly decreased by the RO-[C]R' component. Other studies<sup>13</sup> in our laboratory indicate that the  $\eta$  contribution of the components decreases in the following sequence: R(CN)- $\phi$ R' > R-(Cl)OOC $\phi$ R' > ROSOR' > RO-OR' > RO-OOCR' > ROSR' > RO-R' > RO-[C]R'. The dielectric anisotropy of the mixtures is most affected by the strongly negative o-cyano R(CN)- $\phi$ R' component, by the negative

RO-[C]R' components, and by the strongly positive R-(Cl)OOC $\Phi$ R' component; we estimate the  $\Delta\epsilon$  of these ester classes to be approximately -3.7, -1.3, and 5.5, respectively. The conductivity anisotropy of the redox dopant is approximately the same in four of the mixtures, but is distinctly lower in the HRL-2N52 and HRL-26N3 mixtures.

The DS threshold voltages ( $V_{th}$ ) for these redox-doped mixtures are summarized in Figure 2, which shows the effect of surface alignment,  $\Delta\epsilon$ , and the use of ac and dc voltages. The effect of  $\Delta\epsilon$  on the ac thresholds (both surface- $\parallel$  and surface- $\perp$ ) is similar to that reported<sup>14</sup> for other LC mixtures. The same type of effect is seen here for the dc- $V_{th}$  which are at lower voltages, although the dc- $V_{th}$  values are less reproducible than the ac- $V_{th}$  values. The general effect of  $\Delta\epsilon$  on  $V_{th}$  is observed despite the compositional differences in these ester mixtures, probably because all of the mixtures are esters with some common components and similar  $\sigma_{\parallel}/\sigma_{\perp}$  values, as well as similar clearpoints. The mixtures with the best dc- $V_{th}$  values are HRL-25N4 and HRL-256N5, each of which contains thioester components.

The dc-DS curves of scattering (where % S = 100 - % T) versus voltage are shown in Figure 3 for the six mixtures in surface- $\parallel$  cells. A gradual increase in the scattering levels between their  $V_{th}$  and about 10 to 12 V is considered a favorable feature for achieving a gray scale capability in pictorial matrix displays. The DS response times generally increase as the viscosity of the mixtures increase, as shown in Figure 4 where the on-time is the sum of the delay time and the rise time. The mixtures with the fastest response times are those with the lowest viscosities, namely HRL-26N3 and HRL-24N4.

#### Properties at Elevated Temperatures

The effects of elevated temperatures are determined for several anisotropic properties of these mixtures. The flow viscosities in the

25° to 65°C range are shown in Figure 5. They all follow similar patterns and have relatively larger  $\eta$  values at the lower temperatures than would be expected from a linear plot of  $\log \eta$  versus  $T^{-1}$ . This may be related to some cybotactic nematic characteristics, as discussed below. The temperature dependence of  $\Delta\epsilon$  and  $\epsilon_{\perp}$  is shown in Figures 6 and 7. The only unusual effect is that the  $\Delta\epsilon$  of HRL-26N3 changes from slightly positive at room temperature to slightly negative between 50°C and its clearpoint. Three of the mixtures (HRL-2N52, -25N4, and -26N3) show relatively small changes in their  $\Delta\epsilon$  values between 20° and 60°C. The effect of temperature on  $\sigma_{\parallel}/\sigma_{\perp}$  is shown in Figure 8. As mentioned above, four of the mixtures have fairly high  $\sigma_{\parallel}/\sigma_{\perp}$  values of 1.40 to 1.45 at 25°C while HRL-26N3 and HRL-2N52 have smaller conductivity anisotropies. The latter two mixtures also show the most evidence of cybotactic nematic character<sup>15</sup> (short-range smectic order) at lower temperatures, as indicated by the increase of  $\sigma_{\parallel}/\sigma_{\perp}$  with increasing temperature to give a maximum  $\sigma_{\parallel}/\sigma_{\perp}$  value.<sup>16</sup> The cybotactic nematic effects cause lower  $\sigma_{\parallel}/\sigma_{\perp}$  values in HRL-26N3, and are responsible for its relatively higher  $V_{th}$  values in surface- $\parallel$  cells at 23°C (Figure 2). The effect of temperature on resistivity is shown in Figure 9, where the spread of  $\rho_{\perp}$  values at a given temperature is caused by differences in the concentration of ions produced by the redox dopants in these LC mixtures. In these plots, the temperature effects on  $\rho_{\perp}$  are roughly parallel for all of the mixtures except HRL-26N3. Its slightly smaller slope is probably related to its strong cybotactic nematic characteristics. In general,  $\rho_{\perp}$  changes by an order of magnitude in the 45° range, between 25° and 70°C. Slightly steeper plots of this type are obtained for the apparent dc-resistivity of these mixtures in surface- $\parallel$  cells when DS is activated with 20 Vdc. In the latter case, the apparent  $\rho_{dc}$  changes by an order of magnitude in the 36° range, between 35° and 71°C. This latter range corresponds to the practical temperature range of operating a pictorial matrix display cell if the  $\rho_{dc}$  of the LC in it has to be maintained between  $10^9$  and  $10^{10}$   $\Omega$ -cm.

This is the approximate  $\rho_{dc}$  range required in a matrix display, so that at 71°C the charge on each pixel capacitor does not leak off too fast in 1/30 a sec frame time (i.e.  $\rho_{dc} > 10^9 \Omega\text{-cm}$ ). And, so that at 35°C, the LC is conductive enough to show good DS (i.e.,  $\rho < 10^{10} \Omega\text{-cm}$ ).

#### Dynamic Scattering at Elevated Temperatures

The dc-DS curves of scattering versus voltage have several characteristic changes at elevated temperature, but as shown in Figures 10 and 11, the effects are not large. In general the dc- $V_{th}$  decreases as the temperature increases; and at higher temperatures the scattering levels are relatively better in the voltage range below 10 V, and poorer in the voltage range above 10 V. The temperature effects on DS do not appear to be strongly affected by  $\Delta\epsilon$  changes, since the  $\Delta\epsilon$  of HRL-26N3 changes from about 0.07 to -0.01 in the temperature range in Figure 10, while the  $\Delta\epsilon$  for HRL-26N4 changes from about -1.0 to -0.7 in the similar results shown in Figure 11.

The DS response times are more strongly affected by temperature, as shown in Figure 12 for the three more stable mixtures. The data are presented as  $\log \tau$  versus  $T^{-1}$  to permit comparisons with similar plots of the viscosity (Figure 5) and resistivity (Figure 9) changes with temperature. In the lower temperature range the  $\tau_D$  and  $\tau_{ON}$  decrease with increasing temperature in the same manner as  $\eta$  decreases. But in the upper temperature range, the response times tend to level off and change less with temperature. Nevertheless, the response times are generally faster at higher temperatures, where they are more suitable for displaying TV rate pictures with LC devices. In a TV rate matrix display, it is particularly advantageous to have  $\tau_{ON} < \text{frame time} \leq \tau_D$ , and to have a high  $\tau_D/\tau_{ON}$  ratio at elevated temperatures, where the activating voltage from a pixel capacitor may decrease during the frame time as a result of the increased conductivity of the LC. The HRL-2N52 mixture in Figure 12 shows such a favorable condition at 64°C



with  $\tau_{ON} = 7$  ms and  $\tau_D = 70$  ms, that in a 33.3 ms frame time it reaches nearly full DS in about 1/5 of the frame, and decays fully in a little more than two frames.

#### Thermal Stability at Elevated Temperatures

Many of our thermal stability tests are summarized in Table IV, which shows results from heating samples at an accelerated temperature of 100°C. Four of the mixtures showed excellent stability when heated as bulk samples in evacuated glass test tubes for 2,500 h at 100°C, after first degassing them on a vacuum line with a freeze/thaw technique. The other two mixtures (HRL-25N4 and HRL-246N1) showed no significant change in clearpoint, but showed a small increase in conductivity, and slight yellow coloration in the evacuated tubes. Relatively good stability was shown by all of the mixtures after heating for 3,200 h at 100°C in crimp-sealed Al DSC pans. There was no change in clearpoint, but after removal from the pans, the samples showed substantial decreases in resistivity, and the conductive species produced dc-DS in four of the mixtures. This indicates probable thermal sensitivity to oxygen, since the DSC pans were not evacuated. The decreased resistivity is a serious problem if the ionic species thus generated interfere with the electrochemical reversibility of the LCs when redox dopants are present. Poor stability was found when heating the mixtures (1,980 h at 100°C) as thin LC layers (13  $\mu$ m thick) in unsealed test cells with FG/ITO/IBE glass substrates. Even though heated in a N<sub>2</sub>-flushed oven, all of the unsealed cells showed decomposition in the form of some high melting crystalline products in the LCs. The crystals must be reaction products because their melting points are higher than those of any of the initial components. Some of the products may be LCs since the clearpoint of the remaining LC fluid is increased in each mixture. However, because of the small quantity of the products and the complexity of the initial multicomponent mixtures, we have not yet identified the products.

No crystal formation is observed in the thin-layer test cells that are evacuated and sealed. As indicated in Table IV, three of the mixtures were heated for 2,820 h at 100°C. However, contaminants from the epoxy sealant causes the resistivity of the LCs to decrease substantially. These ionic impurities do not provide good electrochemical stability to the LC, as found by rapid degradation of the undoped LC in the sealed cells at 20 Vdc and 55°C after their long period of heating at 100°C. Other qualitative tests show that crystalline products are not formed in heated evacuated tubes with water added, but that they are formed rapidly in unsealed cells made up on glass substrates (no ITO) heated at 100°C in a N<sub>2</sub>-flushed oven. Bulk samples heated in air do not produce products as rapidly as thin cells with glass substrates. Thus the main thermal instability observed for the undoped LCs appears to result from the presence of both glass surfaces and oxygen.

Studies of the thermal stability of the LC mixtures with redox dopants (DBF and TFM) added are also shown in Table IV. Evacuated tubes containing 1% of the redox dopants were heated for 2,300 h at 100°C. The results indicate that the mixtures with fairly good thermal stability with the redox dopants are HRL-26N3, -26N4, and -2N52. (The stability of HRL-2N52 is implied on the basis of common components with the others, and this has been confirmed by other tests described below.) The HRL-25N4 mixture contains the most thioester components and reacts most rapidly with the redox dopants at 100°C. The HRL-256N5 also contains a thioester and shows some reaction. The reactivity of the HRL-246N1 mixture with the redox dopant is believed to be caused by its biphenyl component, which is the only ester class in HRL-246N1 that is not in HRL-26N3 and -26N4. A well-sealed test cell (FG/ITO/PVA substrates sealed with Type II Abelfilm 539, and evacuated) containing a layer of HRL-2N52 13  $\mu$ m thick with 0.25% redox dopant, showed no crystals or discoloration after 5,430 h of heating at 100°C. Collectively, these results indicate that five of the eight classes of LC esters in Figure 1 have good thermal stability, even in the presence of the redox dopant.

## Electrochemical Stability at Elevated Temperatures

Although we have successfully operated redox-doped LC sealed cells (made with Ablefilm 539) for long periods at 20 Vdc at room temperature, we find that they can be operated for only a few days at 55°C before deposits appear on the ITO electrodes. As mentioned above, this problem arises because the sealant introduces ionic impurities that cause electrochemical degradation even in undoped LCs. Thus, we have tested the electrochemical stability of unsealed cells at 55°C in a N<sub>2</sub>-flushed oven, even though we know that some thermal instability can be expected to occur gradually in these unsealed cells. Typical results are shown in Figure 13 for our three most thermally stable LC/redox mixtures, with a range of DBF/TFM concentrations, and with reflective as well as transmission-type cells. No serious defects appeared in any of the cells until after 1,500 h at 20 Vdc and 55°C. More stable resistivity values are observed in the two cells with reflective Ag electrodes, one of which contained HRL-2N52, and the other HRL-26N4. In general, the electrochemical stability of the three more thermally stable mixtures with redox dopants appears to be fairly good at 55°C, and probably would be much better in evacuated cells made with a non-contaminating sealant.

## CONCLUSIONS

Wide-temperature nematic eutectic mixtures can be made using multiple components from several classes of ester structures, including esters of essentially the same molecular length from different classes. In general, low  $V_{th}$  for DS occurs with high  $\sigma_{||}/\sigma_{\perp}$  and small  $\Delta\epsilon$  values (in surface-|| cells), and fast response is favored by low  $\eta$ . Among the eight ester classes studied in six mixtures, the RO-[C]R', RO-R', and RO $\phi$ R' structures have relatively low  $\eta$  while the R(CN)- $\phi$ R' and R-(Cl)OOC $\phi$ R' structures have relatively high  $\eta$ . Good thermal stability

at 100°C, in the presence of the DBF/TFM redox dopants, is shown in evacuated tubes for three mixtures which include five different classes of esters. Structures having lower stability with redox dopants are the thioesters and a biphenylcarboxylate ester. One of our thermally stable mixtures, HRL-26N3, has the widest nematic range (-20° to 76°) as well as the lowest  $\eta$  and the fastest dc-DS response times of the six mixtures; however, it shows cybotactic nematic characteristics, and has lower  $\sigma_{||}/\sigma_{\perp}$  valued than most of the other mixtures. The temperature dependence of  $\rho_{dc}$  changes approximately on an order of magnitude between 35° and 71°C. Some of the dc-DS characteristics improve at elevated temperatures, notably the  $V_{th}$  decreases, and the  $\tau_{ON}$  becomes short compared to the typical 33 ms frame-time of a matrix display. Relatively good dc-DS operating lifetime is demonstrated at elevated temperatures (>1,500 h at 20 Vdc and 55°C) in unsealed cells. However, accelerated tests at 100°C show that the LCs in unsealed test cells are thermally decomposed by traces of oxygen, and that this instability is catalyzed by glass surfaces. This thermal decomposition is avoided in evacuated cells made with an epoxy film sealant. However, elevated temperatures generate conductivity impurities in the LC from epoxy sealants. These impurities greatly reduce the dc-DS lifetime of the redox-doped mixtures at elevated temperatures, indicating that improved sealants are needed.

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Table I. Thermal Properties of Components

Class Code	Compound Code <sup>a</sup>	Molecular Length, <sup>b</sup> (A)	Melting Point, °C	Clear- point °C	$\Delta H_f$ , Kcal/Mole
RO-R'	20-3	19.67	75.4	65.2	6.26
RO-R'	20-5	22.21	62.8	63.4	7.04
RO-R'	40-6	25.81	39.5	48.2	7.82
RO-R'	60-5	27.03	40.9	59.3	5.54
RO-R'	80-3	26.84	51.8	56.8	6.12
RO-OR'	40-05	26.03	68.6	83.4	5.49
RO-OR'	60-01	23.60	54.9	80.4	6.19
ROSR'	10S5	21.43	63.8	70.6	5.26
ROSOR'	10S04	21.20	74.1	106.9	7.16
ROSOR'	10S06	23.90	65.0	100.1	6.47
RO-OOCR'	10-00C3	20.06	81.0	85.3	7.52
RO-OOCR'	40-00C4	25.40	67.2	83.6	8.19
RO-OOCR'	60-00C5	28.92	50.7	85.6	6.13
RO-[C]R'	20-[C]3	20.21	48.1	78.7	6.48
RO-[C]R'	40-[C]4	23.84	38.4	63.2	3.81
RO-[C]R'	60-[C]5	27.41	30.6	79.8	5.71
R-(C1)OOC:R'	5-(C1)OOC:5	31.03	40.1	122.0	5.15
R(CN)-:R'	7-(CN)-:5	29.72	44.4	103.2	5.23

<sup>a</sup>Where 20-3 refers to p-ethoxyphenyl p-propylbenzoate, etc.

<sup>b</sup>From CPK models of fully extended configurations; see references 10 and 11.

Table II. Composition of Liquid-Crystal Mixtures

Component	Mole Fraction of Component in Mixture <sup>a</sup>					
	<u>2N52</u>	<u>25N4</u>	<u>26N3</u>	<u>26N4</u>	<u>246N1</u>	<u>256N5</u>
20-3	0.093	0.079	0.033	0.108	0.087	0.073
20-5	0.102	0.085	—	0.120	0.094	0.076
40-6	0.189	—	—	—	—	—
60-5	—	0.256	0.147	—	—	—
80-3	—	—	0.086	—	—	—
40-05	0.147	0.127	—	—	—	0.128
60-01	0.168	0.143	0.065	0.194	0.157	0.135
10 <del>S</del> 5	—	0.155	—	—	—	0.142
10 <del>S</del> 04	—	0.057	—	—	—	—
10 <del>S</del> 06	—	0.098	—	—	—	0.094
10-00C3	0.049	—	—	0.058	—	0.041
40-00C4	0.060	—	—	0.073	—	0.049
60-00C5	0.193	—	—	0.223	—	0.120
20-[C]3	—	—	—	0.222	—	0.142
40-[C]4	—	—	0.280	—	—	—
60-[C]5	—	—	0.220	—	0.390	—
5-(C1)00C $\phi$ 5	—	—	0.169	—	—	—
7(CN)- $\phi$ 5	—	—	—	—	0.272	—

<sup>a</sup>Calculated eutectic mixtures, except HRL-256N5, which is determined experimentally.

Table III. Properties of LC Mixtures

Property	Mixture HRL Number					
	<u>2N52</u>	<u>25N4</u>	<u>26N3</u>	<u>26N4</u>	<u>246N1</u>	<u>256N5</u>
Calculated Melting Point, °C <sup>a</sup>	3.0	-0.9	-15.0	6.7	1.3	-
Observed Melting Point, °C <sup>b</sup>	7.0	5.0	-20.0	21.0	19.0	-9.0
Calculated Clearpoint, °C <sup>a</sup>	73.0	74.7	77.5	78.0	83.4	-
Observed Clearpoint, °C	71.9	71.6	75.8	77.0	81.0	77.4
Average Length, Å	24.90	23.92	26.41	23.29	26.28	23.32
$\Delta n$ at 23°C	0.150	0.169	0.118	0.141	0.143	0.158
$\eta$ , at 25°C, cP	64.2	59.2	47.8	49.3	66.6	58.2
$\Delta \epsilon$ at 25°C <sup>c</sup>	-0.48	-0.13	0.07	-0.96	-1.55	-0.51
$\sigma_{II}/\sigma_I$ (Redox) at 25°C <sup>d</sup>	1.28	1.45	1.33	1.40	1.42	1.44

<sup>a</sup>For calculated eutectic mixture.

<sup>b</sup>Approximate temperature at which all crystals melted.

<sup>c</sup>Measured at 5 kHz.

<sup>d</sup>Measured at 100 Hz.



Table IV Thermal Stability Tests

Conditions and Measurements <sup>a</sup>	HRL Mixtures and Results					
	2N52	25N4	26N3	26N4	246N1	256N5
<u>Undoped</u>						
<u>Initial (no heating)</u>						
Clearpoint	71.5°	71.6°	75.9°	76.3°	80.7°	77.4°
$\rho \times 10^{-10}$	19.9	10.8	10.6	12.3	254	17.6
<u>2,500 h at 100°C, Evacuated tubes<sup>b</sup></u>						
Clearpoint <sup>c</sup>	71.7°	72.0°	75.9°	76.2°	80.8°	77.2°
$\rho \times 10^{-10}$	15.6	5.63	9.44	16.3	2.41	14.5
Visual Change	none	yellow	none	none	yellow	none
<u>3,200 h at 100°C, DSC pans<sup>d</sup></u>						
Clearpoint <sup>c</sup>	69.9°	70.1°	75.3°	75.1°	78.8°	76.8°
$\rho \times 10^{-10}$	0.40	0.35	0.31	0.29	0.31	0.26
DS at 20V dc	yes	yes	no	no	yes	yes
<u>1,980 h at 100°C, unsealed cells (N<sub>2</sub>)<sup>e</sup></u>						
Clearpoint (LC part only)	74.3°	72.2°	80.1°	81.4°	84.1°	80.6°
Melting Points of crystals in LC	112° to 133°	100° to 134°	137° to 173°	103° to 159°	115° to 169°	81° to 176°
$\rho \times 10^{-10}$	0.33	2.18	0.70	0.42	0.85	0.52
<u>2,820 h at 100°C, sealed cells<sup>f</sup></u>						
$\rho \times 10^{-10}$	-	0.35	0.28	-	0.38	-
Crystals	-	none	none	-	none	-
<u>1% Redox Doped</u>						
<u>Initial (no heating)</u>						
Clearpoint	-	67.5°	72.0°	71.7°	76.7°	72.5°
$\rho \times 10^{-8}$	-	17.7	29.0	6.81	17.5	20.0
<u>2,300 h at 100°C, Evacuated tubes<sup>b</sup></u>						
Clearpoint	-	67.1°	72.1°	71.6°	76.4°	72.7°
$\rho \times 10^{-8}$	-	6.22	8.98	5.43	5.52	3.71
Visual Change	-	Dark ppt.	none	none	Dark color	Dark color

<sup>a</sup>Temperature in °C,  $\rho$  in  $\Omega$ -cm at 100 Hz and 23° in surface -  $\pi$  cell.

<sup>b</sup>Pyrex tubes.

<sup>c</sup>No crystals observed.

<sup>d</sup>Crimp-sealed Al pans.

<sup>e</sup>N<sub>2</sub>-flushed oven. Cells are FG/ITO/IBE.

<sup>f</sup>Sealed with Ablefilm 539, Type II. Cells are FG/ITO/PVA.

STRUCTURE CLASS	CLASS CODE
$\text{RO}-\text{C}_6\text{H}_4-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{C}_6\text{H}_4-\text{R}'$	RO-R'
$\text{RO}-\text{C}_6\text{H}_4-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{C}_6\text{H}_4-\text{OR}'$	RO-OR'
$\text{RO}-\text{C}_6\text{H}_4-\text{S}-\overset{\text{O}}{\parallel}\text{C}-\text{C}_6\text{H}_4-\text{R}'$	RO-S-R'
$\text{RO}-\text{C}_6\text{H}_4-\text{S}-\overset{\text{O}}{\parallel}\text{C}-\text{C}_6\text{H}_4-\text{OR}'$	RO-S-OR'
$\text{RO}-\text{C}_6\text{H}_4-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{C}_6\text{H}_4-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{R}'$	RO-OOCR'
$\text{RO}-\text{C}_6\text{H}_4-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{C}_6\text{H}_3(\text{H})-\text{R}'$	RO-[C]R'
$\text{R}-\text{C}_6\text{H}_4-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{C}_6\text{H}_3(\text{Cl})-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{C}_6\text{H}_4-\text{R}'$	R-(Cl)OOC $\phi$ R'
$\text{R}-\text{C}_6\text{H}_3(\text{CN})-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{R}'$	R(CN)- $\phi$ R'

Figure 1. Structure and code symbols for the classes of LC ester components studied in mixtures.

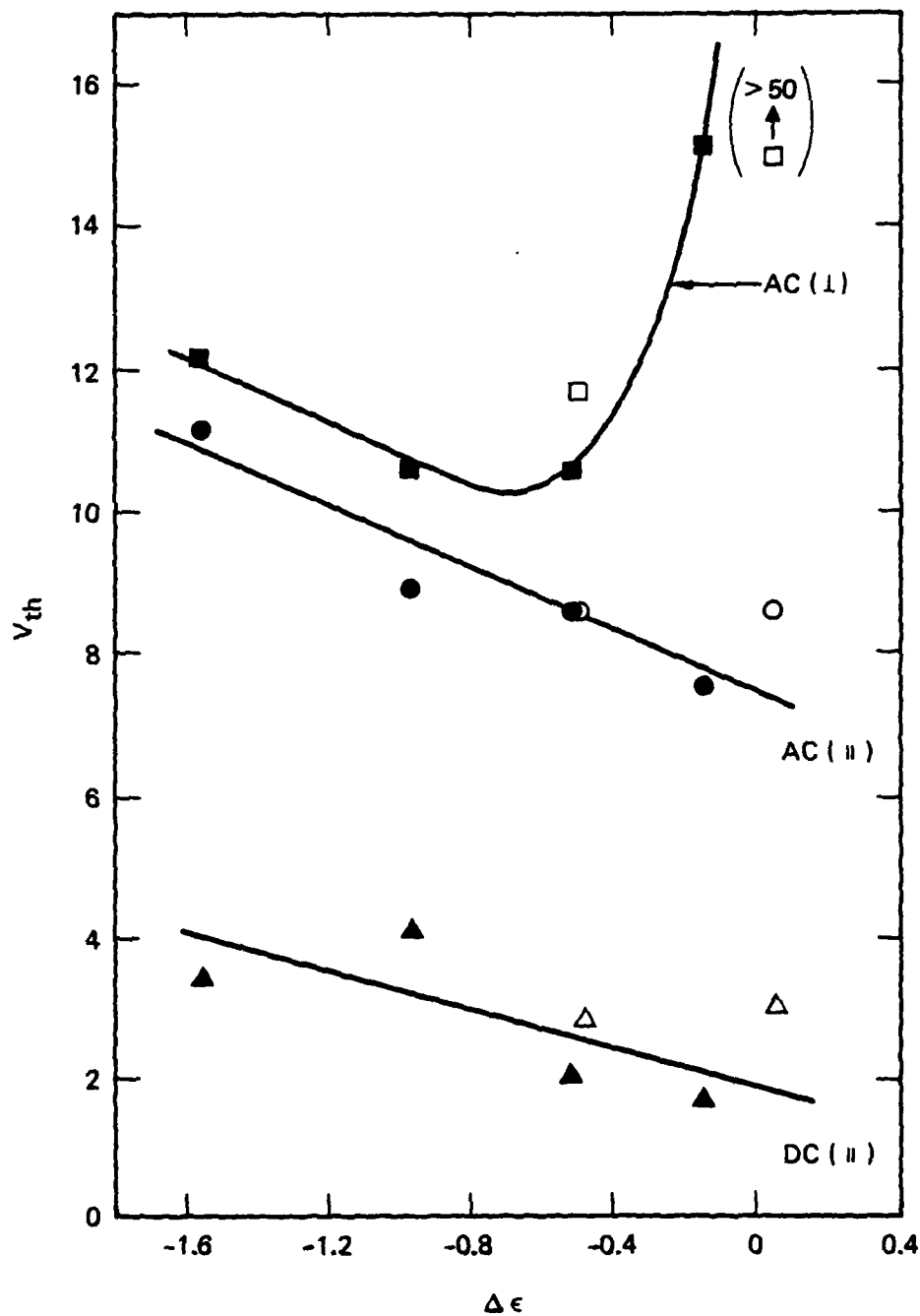


Figure 2. Effect of parameters on DS- $V_{th}$  of redox-doped mixtures. (Transmission cells,  $13 \mu\text{m}$  thick,  $23^\circ\text{C}$ , 0.5% DBF/TFM. Dark points have  $\sigma_{II}/\sigma_I$  in 1.40 to 1.45 range.)

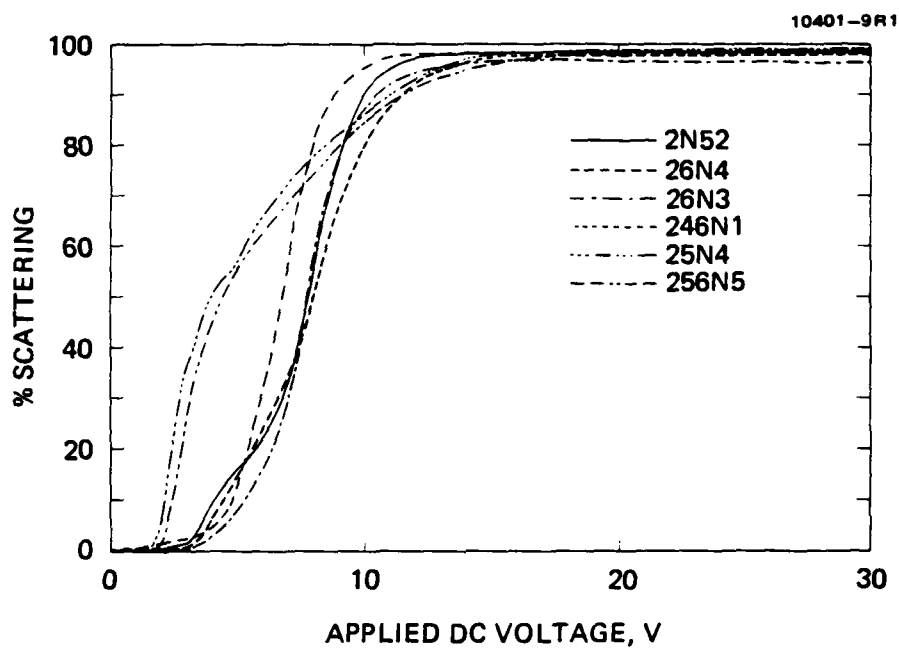


Figure 3. DS curves of redox-doped mixtures. (Transmission cells, 8.4  $\mu\text{m}$  thick, surface-||, 23°C, 0.5% DBF/TFM).

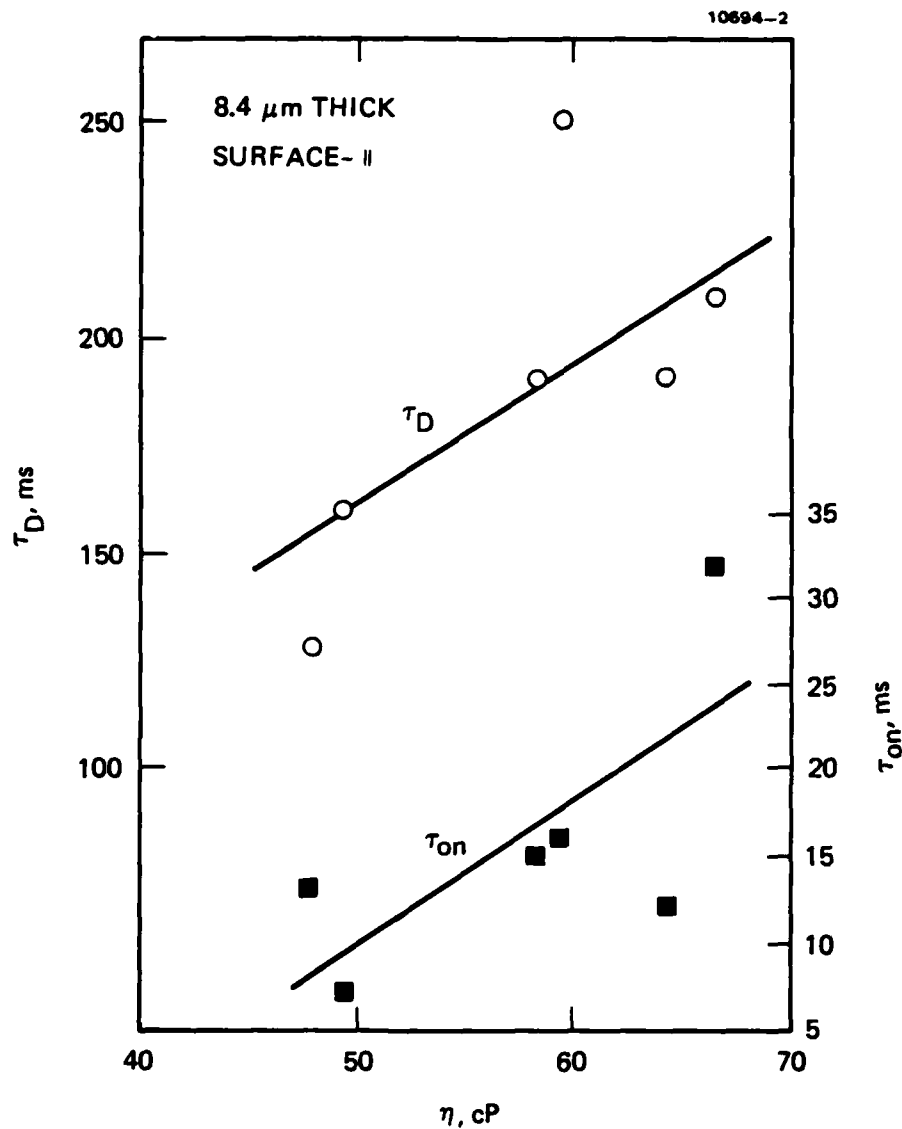


Figure 4. Viscosity effect on response times. (20 Vdc, 0.5% DBF/TFM, 25°C,  $\tau_D$  = decay time from 100 to 10% S,  $\tau_{ON}$  = time from 0 to 90% S.)

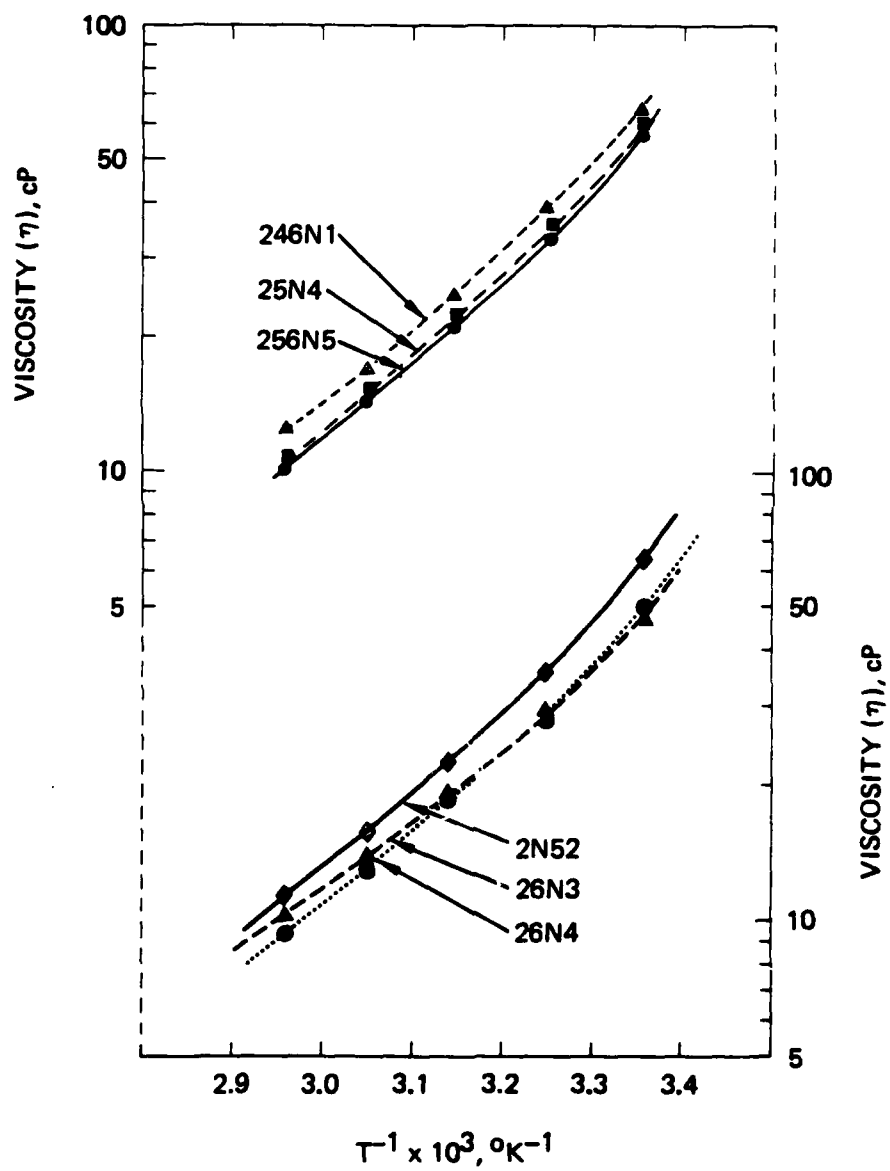


Figure 5. Flow viscosity of undoped mixtures.

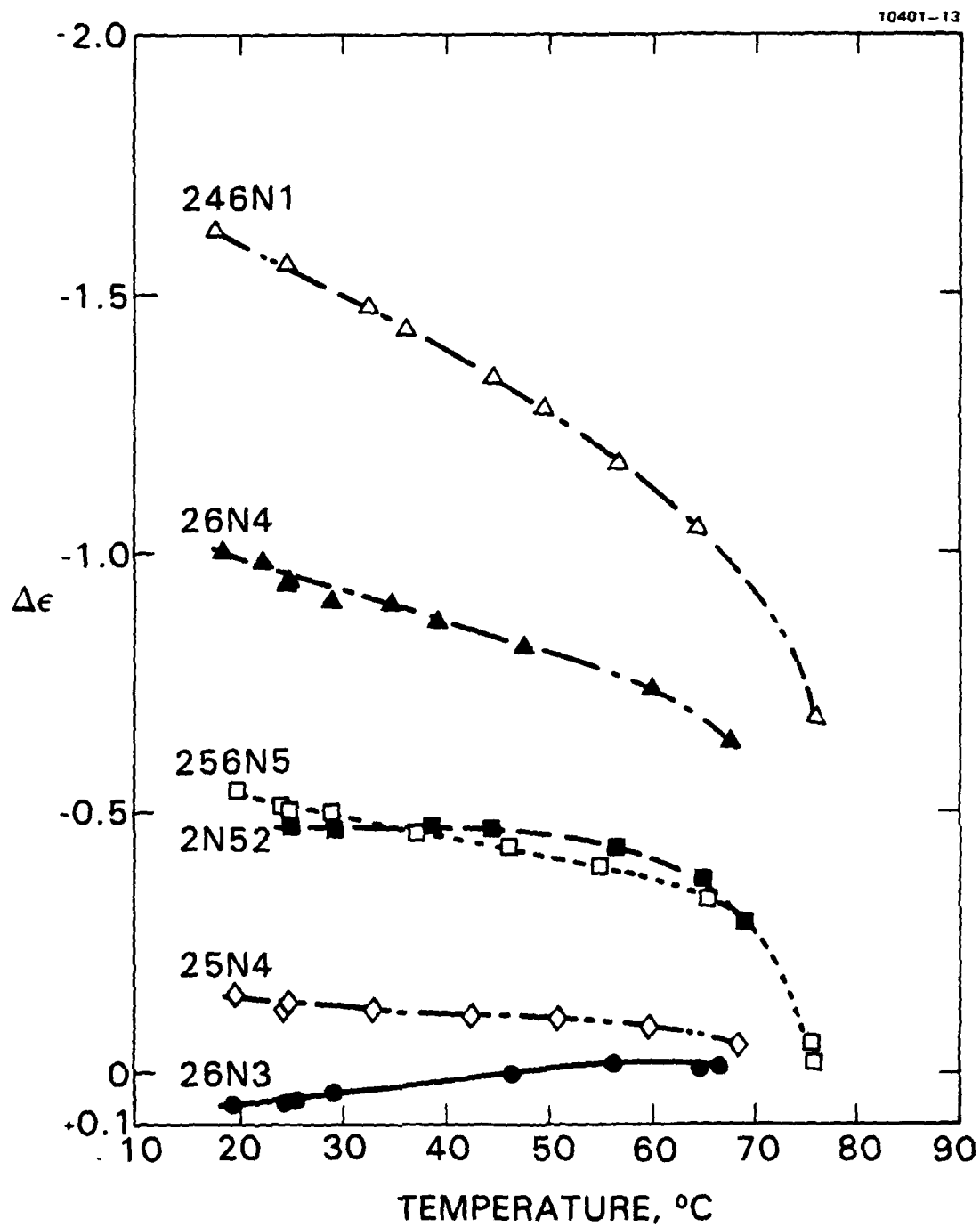


Figure 6. Effect of temperature on dielectric anisotropy of redox-doped mixtures (0.5% DBF/TFM).

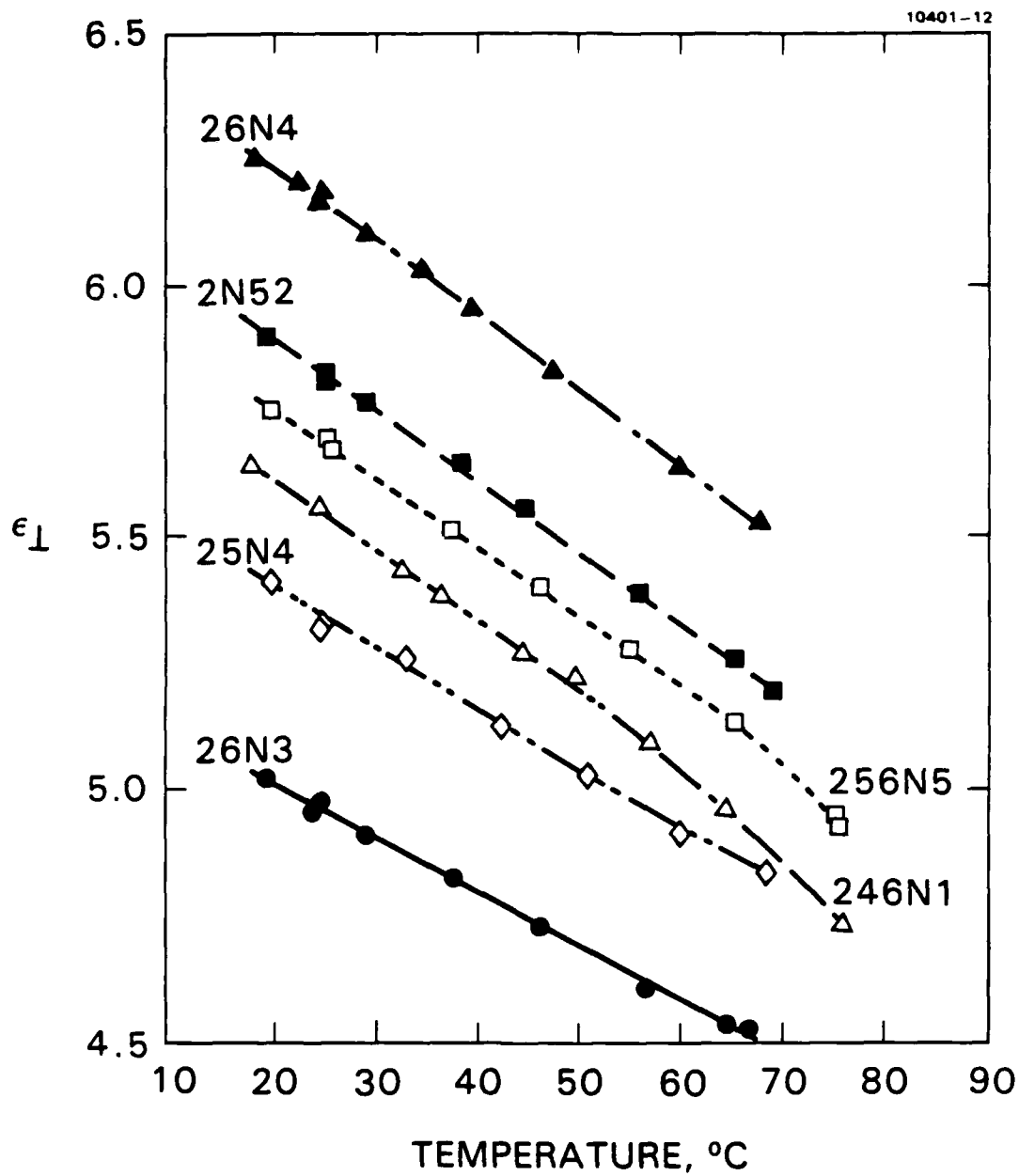


Figure 7. Effect of temperature on the  $\epsilon_{\perp}$  dielectric constant of redox-doped mixtures (0.5% DBF/TFM).



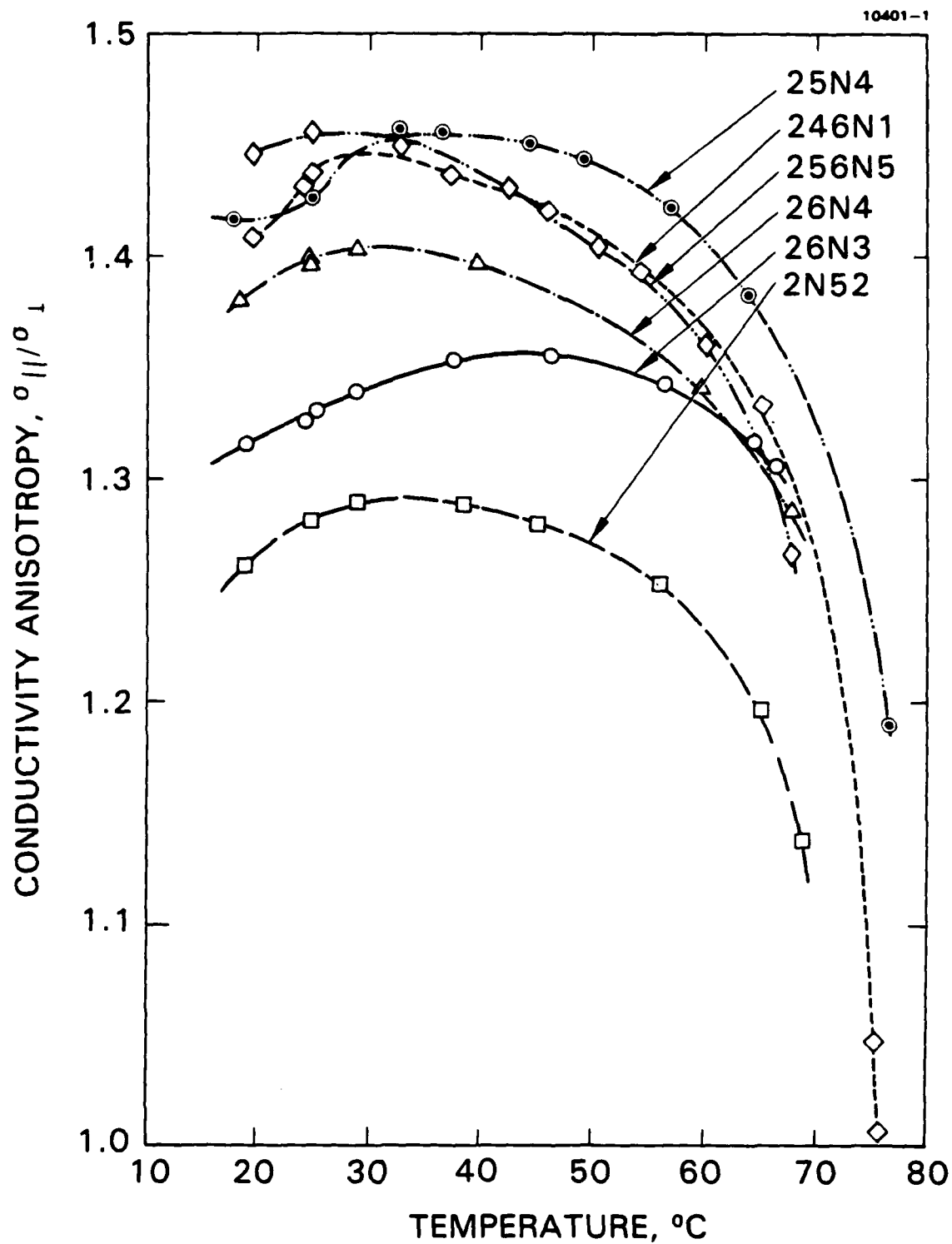


Figure 8. Effect of temperature on the  $\sigma_{||}/\sigma_{\perp}$  of redox-doped mixtures (0.5% DBF/TFM).

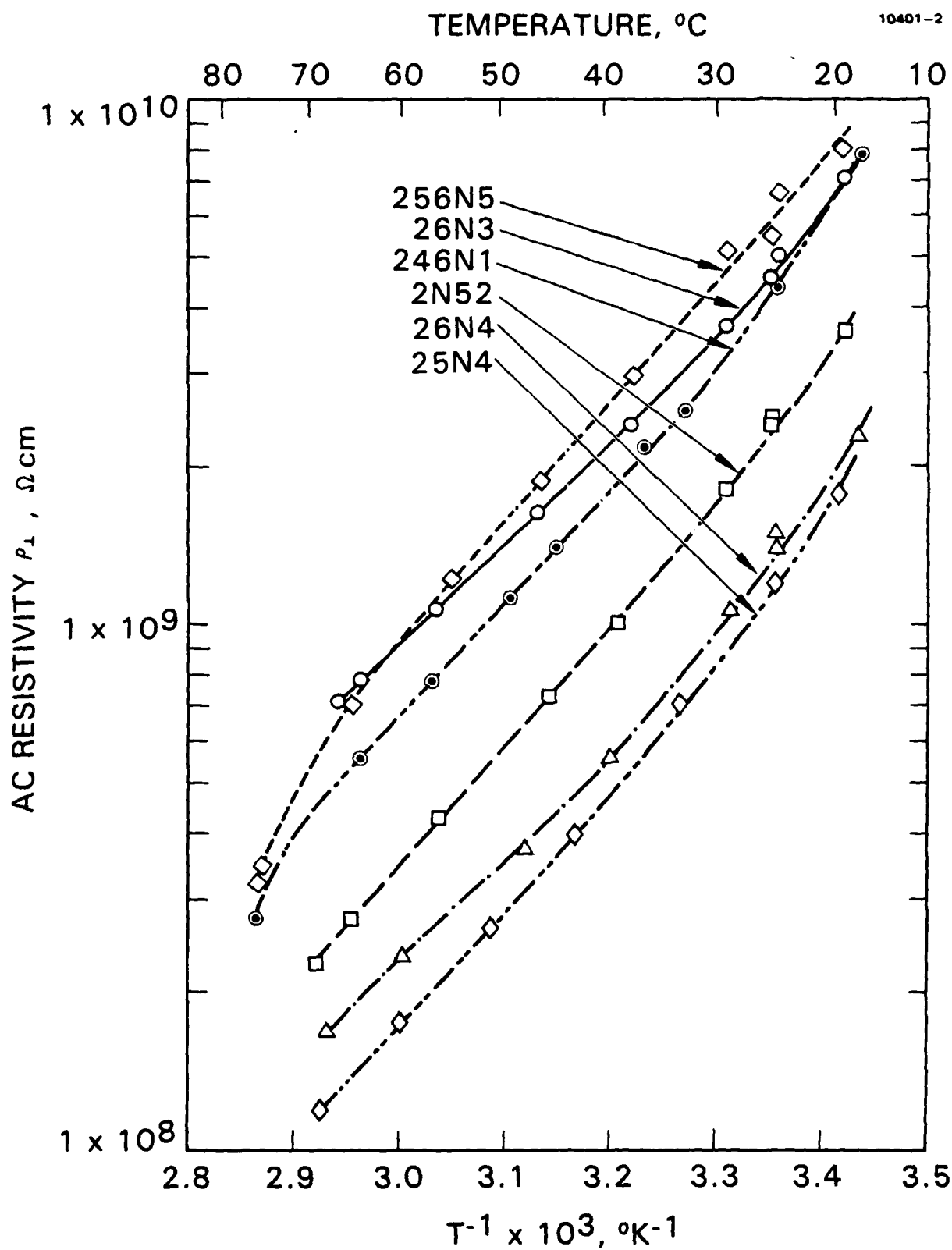


Figure 9. Effect of temperature on resistivity of redox-doped mixtures (0.5% DBF/TFM).

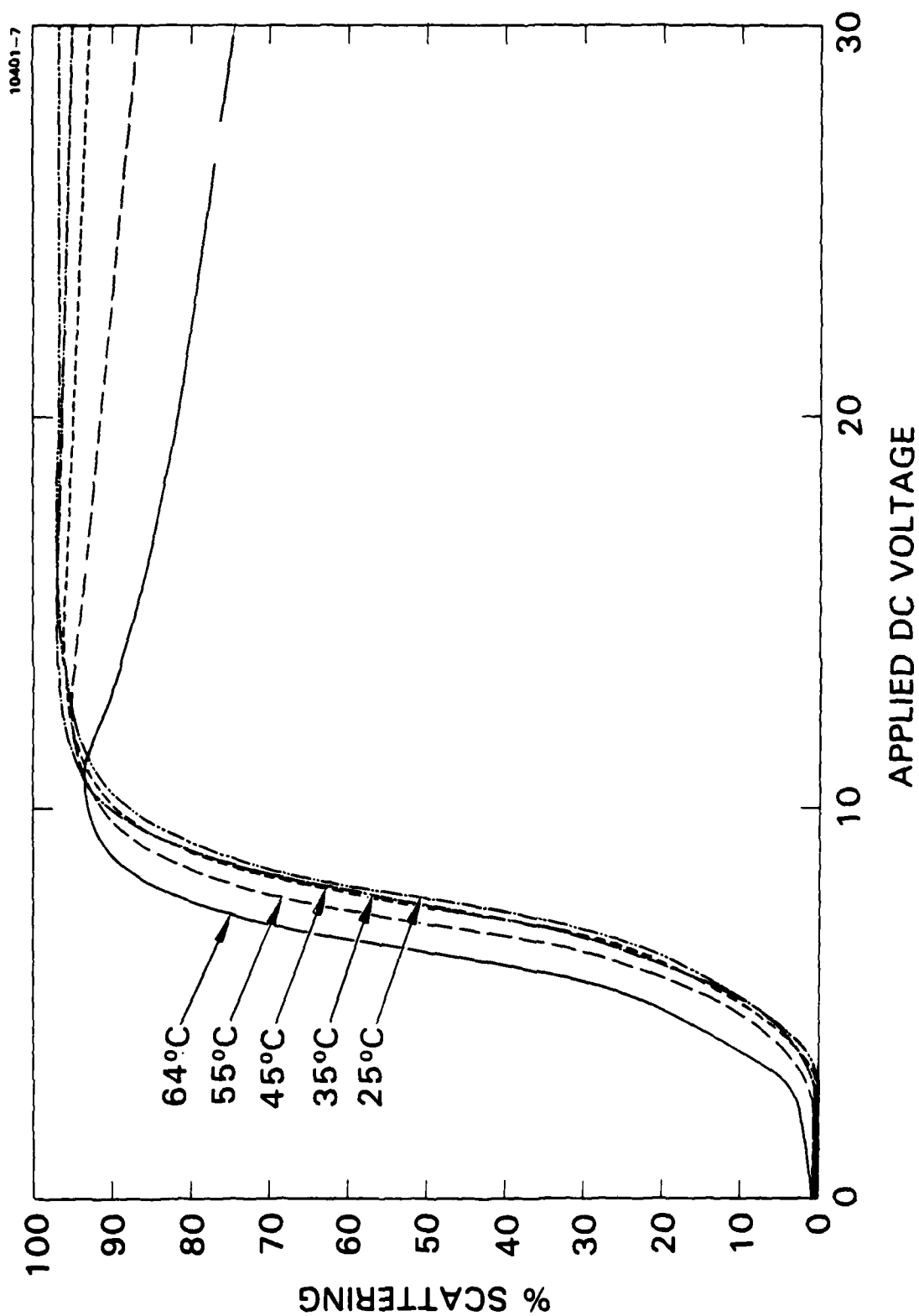


Figure 10. Temperature effect on dc-DS curves of redox-doped HRL-26N3. (Surface-II, 8.4  $\mu\text{m}$  thick, 0.5% DBF/TFM.)

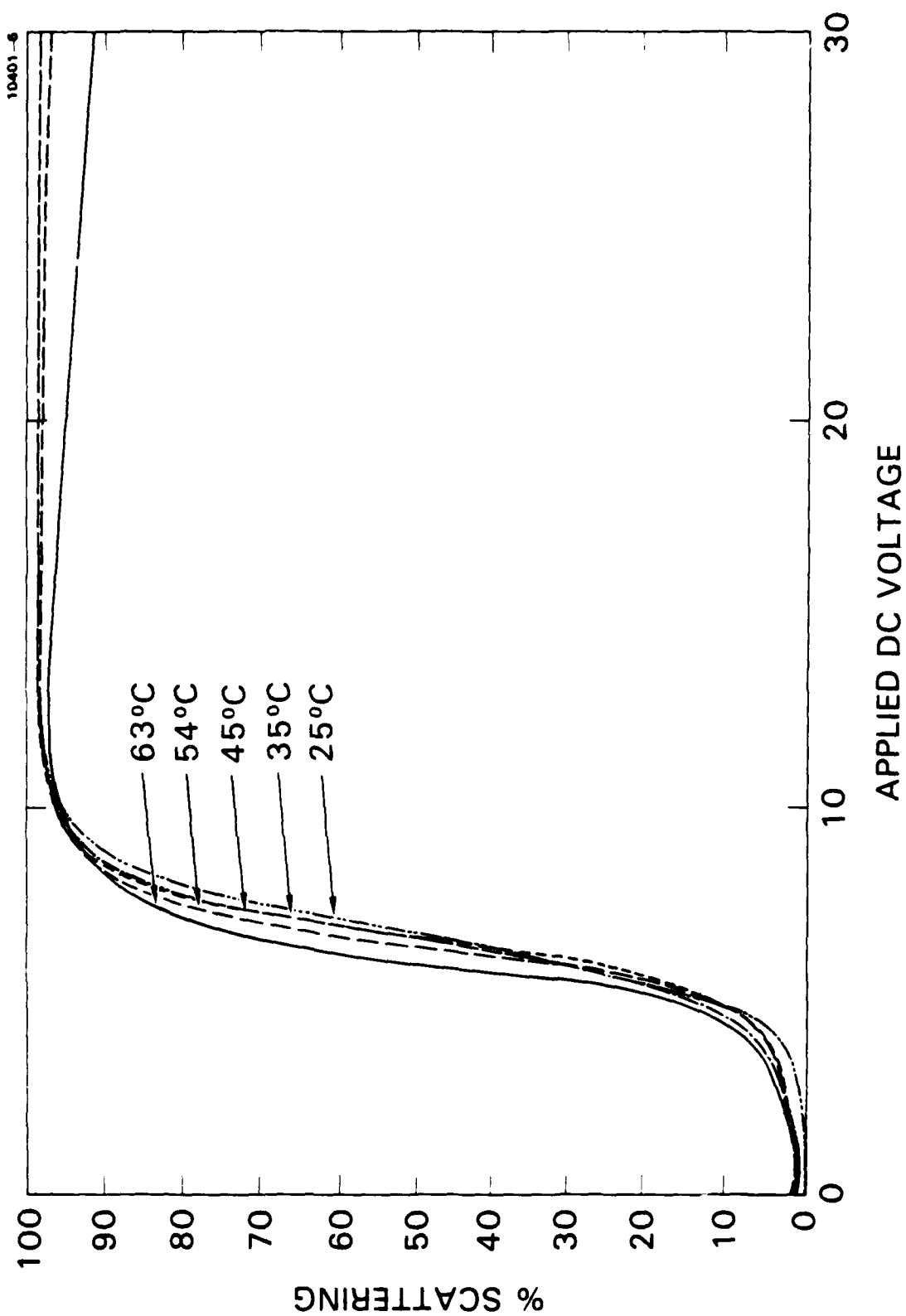


Figure 11. Temperature effect on DS curves of redox-doped HRL-26N4. (Surface-II, 8.4  $\mu$ m thick, 0.5% DBF/TFM.)

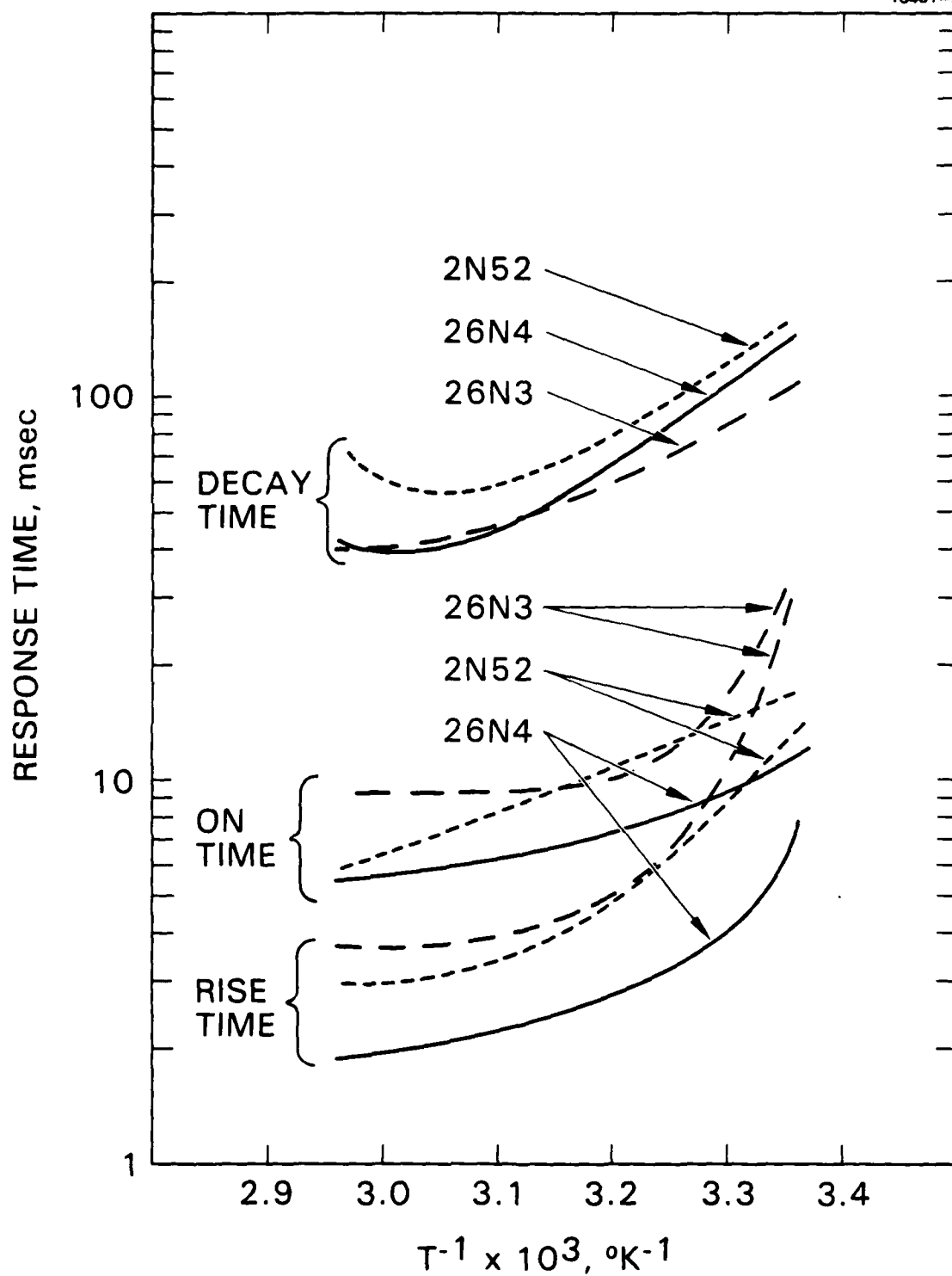


Figure 12. Effect of temperature on dc-DS response times from 15 V dc. (0.5% DBF/TFM, 8.4  $\mu m$  thick, surface-||.)

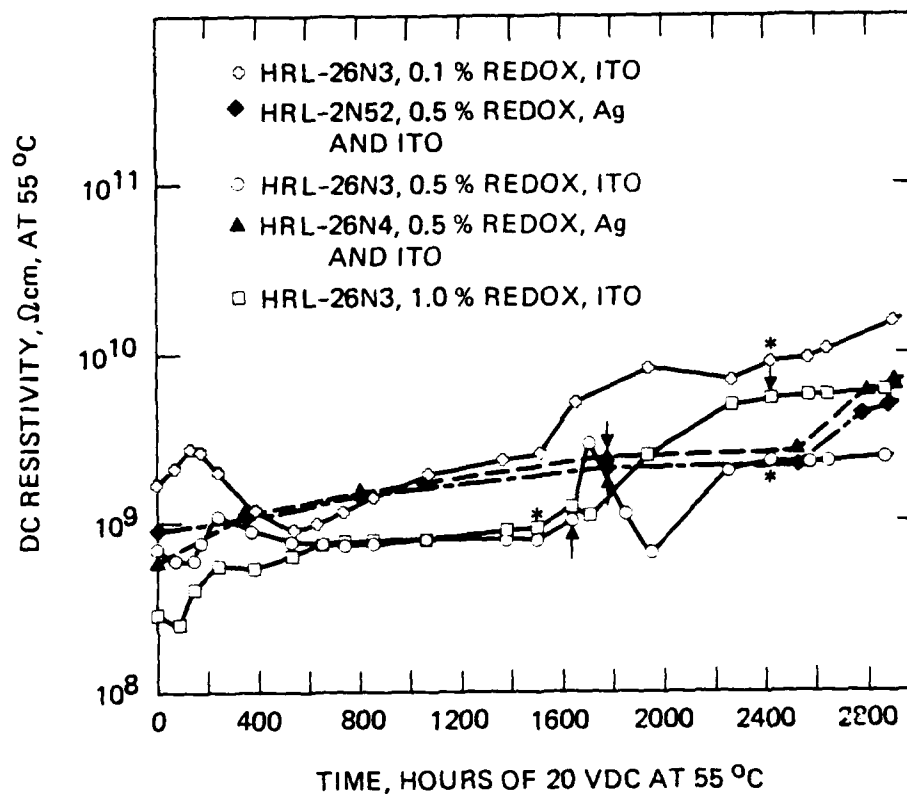


Figure 13. Electrochemical stability of DS at 55°C. (Unsealed cells,  $\text{N}_2$ , 13  $\mu\text{m}$  thick, surface-||, PVA coated except 26N3 with 0.5% redox. The \* indicates crystals at 23°C; the + is brown spots or ppt.)

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